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# Oxygenates for Advanced Petroleum-Based Diesel Fuels

## INTERIM REPORT TFLRF No. 357

by  
**David W. Naegeli**  
**Stan Moulton**  
**Edwin C. Owens**  
**Edwin A. Frame**

**U.S. Army TARDEC Fuels and Lubricants Research Facility (SwRI)**  
**Southwest Research Institute**  
**San Antonio, TX 78228-0510**

Under Contract to  
**U.S. Army TARDEC**  
**Petroleum and Water Business Area**  
**Warren, MI 48397-5000**

for  
**U. S. Department of Energy**  
**Office of Transportation Technologies**  
**1000 Independence Avenue, SW**  
**Washington, D. C. 20585**

and  
**Coordinating Research Council, Inc.**  
**3650 Mansell Road, Ste. 140**  
**Alpharetta, GA 3022-3068**

Contract Nos. DAAE-07-99-C-L053 (WD03 of SwRI Project No. 03-3227)  
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February 2001

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Edwin C. Owens, Director  
U.S. Army TARDEC Fuels and Lubricants  
Research Facility (SwRI)



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13. ABSTRACT (Maximum 200 words)  Oxygenates for diesel fuel are organic compounds such as alcohols, ethers and ketones that contain a relatively high concentration of oxygen. The purpose of adding oxygenates to diesel fuel is to reduce the emissions of particulate matter (PM) in the exhaust. The goal of this project was to select two candidate oxygenate compounds that will be used in a full-scale engine test program to determine which oxygenate will give the greatest improvement in exhaust emissions and performance when blended with conventional diesel.  The literature was reviewed for impact of oxygenates on PM emissions, to compile oxygenate properties, and select test fuel oxygen level. A hypothesis of the mechanism of oxygenate effect on PM formation was developed. Physicochemical properties of oxygenate candidates were collected. Property data was used to screen oxygenates for use in diesel fuel. Oxygenates were ranked according to toxicity and biodegradability.  The economics of oxygenate production was estimated. Eight oxygenates were selected for making oxygenate diesel fuel blends for emission testing in a 2.2L diesel engine at a single operating condition (Mode 6). The two most promising oxygenates were recommended for making oxygenate diesel fuel blends for future emission testing.			
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## **EXECUTIVE SUMMARY**

The summarized objectives, approach, and accomplishments for this project as presented below:

### **Objectives**

- Assess the benefits and limitations of oxygenated diesel fuels on engine performance and emissions.
- Identify oxygenates for exhaust emissions and performance testing based on physico-chemical properties, toxicity, biodegradability, and projected cost of production
- Select at least two oxygenated compounds for advanced engine testing.

### **Approach**

- Review the oxygenate literature to identify potential candidates
- Select oxygenate candidates on the basis of:
  - Oxygen content, flash point, solubility in low aromatic diesel fuel, and stability.
  - Fuel properties such as viscosity, cetane number, and lubricity.
  - Elastomer compatibility
  - Results of a single mode emissions and performance test in a DaimlerChrysler OM611 CIDI engine
  - Potential toxicity, biodegradability, and air quality
  - Economics of producing the most technically promising oxygenates for diesel fuel
- Based on the above criteria, two oxygenate candidates will be selected for multimode testing of engine performance and exhaust emissions in the 2.2L DaimlerChrysler OM611 CIDI engine.

### **Accomplishments**

- A literature search on the effect of oxygenate compounds on particulate emissions from diesel engines was performed.

## **FOREWORD/ACKNOWLEDGMENTS**

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## SYMBOLS AND ABBREVIATIONS

ASTM	American Society for Testing and Materials
bhp	Brake Horse Power
BLE	Butyl lactate ester
BMEP	Brake Mean Effective Pressure
CARB	“pseudo” California Reference Fuel
CIDI	Compression Ignition, Direct Injection
CO	Carbon Monoxide
CO <sub>2</sub>	Carbon Dioxide
COTR	Contracting Officer’s Technical Representative
CRC	Coordinating Research Council
DA	Decanoic Acid
DBM	Di-butyl maleate
DEA	Di-ethyl adipate
DEM	Di-ethyl maleate
DENOX	Nitrogen Oxide After-Treatment Device
DF-2	Reference No. 2 Diesel Fuel
DEE	Diethyl ether
DGME	Di-propylene glycol mono-methyl ether
DI	Direct Injection
DMA	Di-methyl acetal
DME	D-methyl ether
DMM	Dimethoxymethane
DOE	Department of Energy
ECE	
EEA	2-Ethoxy ethyl acetate
EEE	2-Ethoxy ethyl ether
EUDC	
EGR	Exhaust Gas Recirculation
EPA	Environmental Protection Agency
EtOH	Ethanol

## **SYMBOLS AND ABBREVIATIONS (CONTD)**

ETBE	Ethyl tert-butyl alcohol
FT	Fischer-Tropsch
FSG	
FTP	Federal Test Procedure
GTB	Glycerin tri-butyrat
GM	Glycol di-methyl ether
HC	Hydrocarbon
HD	
HSDI	High Speed Diesel Injection
IDI	
MGME	1-Methoxy-2-propanol
MTBE	Methyl tertiary butyl ether
NO <sub>x</sub>	Nitrogen Oxides
OA	Octyl alcohol
PM	Particulate Matter
PME	Palm oil methyl ester
RPM	Revolutions per Minute
RSME	Rape-seed methyl ester
SI	Spark Ignition
SLS	Swedish Low Sulfur
SME	Soybean methyl ester
SOF	Soluble Organic Fraction
SwRI	Southwest Research Institute
TAME	Methyl tert-amyl ether
TARDEC	Tank-Automotive Research Development and Engineering Center
TBA	Tert-butyl alcohol
TBE	2-tertiary butoxy ethanol
TFLRF	U.S. Army TARDEC Fuels and Lubricants Research Facility
TGME	Tri-propylene glycol mono-methyl ether
TPE	Tri-propylene glycol mono-methyl ether
TVF	Total Volatile Fraction

## **1.0 INTRODUCTION**

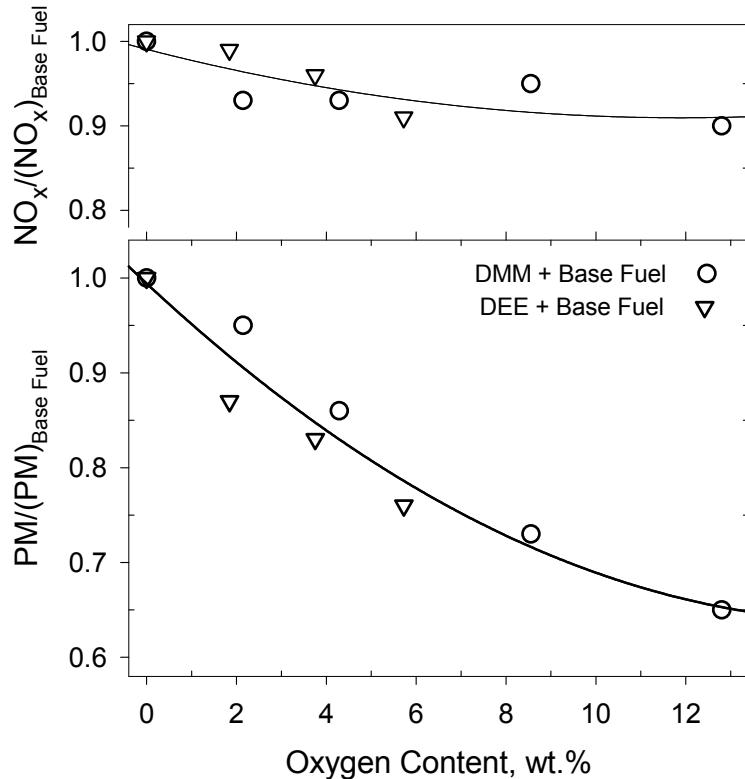
As worldwide energy demand rises, oil consumption will eventually outpace discovery [1-3]\*. Unless infrastructures for alternative energy sources are developed in a timely manner, serious fuel shortages could result. To forestall a possible crisis and allow more time to make a smooth transition to alternative energy sources, it is necessary to develop vehicles that are more efficient. The diesel engine is of particular interest because it is much more efficient than its spark ignited counterpart. However, widespread use of diesel power is restricted by unacceptable exhaust emissions. Developers of the diesel engine have made considerable progress in reducing harmful exhaust emissions. Combustion efficiency has been greatly improved through ultra-high pressure fuel injection and better fluid-flow. Electronic control has been used to optimize engine performance and lower exhaust emissions. Nevertheless, the diesel engine has yet to meet the very stringent emissions standards required by the EPA in the next decade.

The crux of the problem is that the particulate (smoke) emissions are still too high. Since no obvious modifications to the engine design remain to further reduce particulate emissions, the industry is forced to resort to expensive after treatment schemes to oxidize and filter particulate matter, PM, from the exhaust. To alleviate the problem, workers have turned to the development of cleaner burning fuels. Future diesel fuels will be virtually free of sulfur. Sulfur has to be removed from the fuel because it degrades catalytic activity in after treatment devices. Sulfur is removed by “hydrotreating”, which also increases hydrogen to carbon ratio, lowers aromatics and raises cetane number. Low sulfur fuels can yield lower PM emissions because of the increased hydrogen to carbon ratio and the absence of sulfates.

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**\*Numbers in brackets represent references at the end of the document.**

Further reformulation of diesel fuel may involve addition of oxygenates. Several exhaust emissions studies have shown that using oxygen-containing fuels such as methanol and dimethyl ether as diesel fuels substantially reduce PM exhaust emissions. A number of other studies report that blending oxygenates into diesel fuel will also significantly reduce PM emissions in diesel exhaust.[?] Figure 1 shows the effects of dimethoxymethane, DMM, and diethyl ether, DEE, blended with a CARB certified DF-2 on the PM and NOx emissions from a Cummins 5.9L turbodiesel. These results of Cheng and Dibble [4] represent an average of nine operating modes. Figure 1 shows that the emissions benefit of blending oxygenates with diesel fuel goes beyond that explained by simple dilution. This disproportionate reduction in PM emissions is not observed when simply blending in "clean" hydrocarbon compounds. Several studies with results similar to that in Figure 1 show that it is primarily the added oxygen that suppresses the formation of soot or PM during combustion. However, there are claims in the literature that some oxygenates of different molecular structure are more effective in reducing PM emissions than others are.[?]



**Figure 1. Effect of Oxygen Content on the Relative PM and NOx emissions from DMM and DEE Diesel Fuel Blends. Cheng and Dibble, SAE Paper 1999-01-3606.**

The impact and the limitations of oxygenates on the diesel combustion process have not been well defined. Questions on the importance of molecular structure and the maximum achievable PM reduction with oxygenate blends is difficult to quantify because the emissions data in the literature are from several engine types and different operating conditions. The purpose of the present study is to establish criteria for the selection of oxygenates and then evaluate several oxygenates on an equal basis, i.e., in the same engine under the same operating conditions.

## **2.0 BACKGROUND**

Several studies have shown significant reductions in PM emissions from diesel engines when oxygenates were blended with conventional diesel fuels.[?] The mechanism for the effect of oxygenates on soot formation is not known. Well before there was an interest in oxygenates, fuel properties such as hydrogen to carbon ratio, aromatic content, and the number of carbon – carbon bonds were used as correlating parameters for soot formation in hydrocarbon flames. Results from a gas turbine combustor “stirred reactor” [5] showed that exhaust smoke and flame radiation correlated most favorably with hydrogen to carbon ratio. This correlation of soot formation with H to C ratio persisted despite wide variations in molecular composition, volatility and viscosity. While the continuous “steady-state” combustion in a well-stirrer reactor is relatively independent of fuel-air mixing, diesel combustion is transient and less turbulent so properties such as boiling point, viscosity and cetane number can affect the soot forming process. Boiling point affects vaporization, viscosity affects atomization, and cetane number relates to ignition delay, which is the time allowed for mixing before combustion begins.

Various types of oxygen containing compounds including ethers, alcohols, carbonates, acetals and esters have been tested in engines to determine the effects of oxygenates on exhaust emissions.[?] The oxygenates listed in Table 1 range from light molecules such as ethanol to heavy methyl esters of vegetable oils with up to 20 carbon atoms.

**Table 1. Oxygenates Cited in Engine Test Literature**

<b>Acronym</b>	<b>Chemical Name</b>	<b>Common Name</b>	<b>Oxygenate Structural Groups</b>
1GM	Ethylene glycol di-methyl ether	Glyme	C-O-C
2GM	Di-ethylene glycol di-methyl ether	Diglyme	C-O-C
3GM	Tri-ethylene glycol di-methyl ether	Triglyme	C-O-C
4GM	Tetra-ethylene glycol di-methyl ether	Tetraglyme	C-O-C
MGME	1-Methoxy-2-propanol		C-O-C & C-OH
DGME	Di-propylene glycol mono-methyl ether		C-O-C & C-OH
TGME	Tri-propylene glycol mono-methyl ether		C-O-C & C-OH
TPE	Tri-propylene glycol di-methyl ether		C-O-C
TBE	2-tertiary butoxy ethanol		C-O-C & C-OH
EEE	2-Ethoxy ethyl ether		$C_2H_5OCH_2CH_2OC_2H_5$
EEA	2-Ethoxy ethyl acetate		$CH_3CO_2CH_2CH_2OC_2H_5$
BLE	Butyl lactate ester		$CH_3CH(OH)CO_2C_4H_9$
DEM	Di-ethyl maleate		$C_2H_5O_2CCH=CHCO_2C_2H_5$
DEA	Di-ethyl adipate		$C_2H_5O_2CCH_2CH_2CH_2CH_2CO_2C_2H_5$
DBM	Di-butyl maleate		O=C-O-C
GTB	Glycerin tri-butylate	Tributyrin	O=C-O-C
DMM	Di-methoxy methane	Methylal	C-O-C
DMA	Di-methyl acetal		C-O-C
DME	Di-methyl ether	Methyl ether	C-O-C
DEE	Di-ethyl ether	Ethyl ether	C-O-C
SME	Soybean methyl ester	Bio-diesel	O=C-O-C
RSME	Rape-seed methyl ester	Bio-diesel	O=C-O-C
PME	Palm oil methyl ester	Bio-diesel	O=C-O-C
EtOH	Ethanol	Ethyl alcohol	C-OH
TBA	Tert-butyl alcohol	t-Butanol	C-OH
OA	Octyl alcohol	Octanol	C-OH
DA	Decanoic Acid		O=C-OH
MTBE	Methyl tertiary butyl ether	MTBE	C-O-C
ETBE	Ethyl tert-butyl ether	ETBE	C-O-C
TAME	Methyl tert-amyl ether	TAME	C-O-C

Engine emissions and performance studies on oxygenates used a variety of test engines, test modes, and diagnostic methods. All of the studies found significant reductions in PM emissions when either pure oxygenates or oxygenate/DF-2 blends were burned in diesel engines. Some of the studies concluded that the molecular structure affected the soot reducing ability of oxygenates, while others claimed the effect was solely due to the oxygen content of the fuel.[?]

McCormick et al. [6] measured transient exhaust emissions from blends of EtOH, OA, DA, and SME in DF-2 burned in a 9.0 Liter, DDC 6V92 and an 11.1 Liter, DDC Series 60 engine. For each oxygenate – DF2 blend, 4 replicate transient tests were performed. Blends of EtOH, OA and SME in DF2 containing 2% oxygen were tested in the DDC Series 60 engine, and blends of OA, DA, and SME containing 1% oxygen were tested in the DDC 6V92 engine.

In the DDC 6V92 engine, the OA blend with 1% oxygen gave the greatest reduction in PM, about 17%. PM was reduced about 15% by the SME blend and about 13% by the DA blend. The EtOH blend with 2 % oxygen gave the largest reduction in PM (37.6%) in the DDC Series 60 engine. The PM reductions were about 20% for SME and about 12 % for OA. The EtOH blend was not tested in the DDC 6V92. Part of the PM reduction in both engines may have been attributed to a lower heat of combustion of the fuel blends, because the engine calibration was not adjusted to compensate for reduced heating value. Although the peak powers were somewhat lower for oxygenate–DF2 blends than for the neat baseline DF-2, the error did not appear that great because oxygenate concentrations in the blends were not substantial. The results of McCormick, et. al. strongly suggest that the soot formation process depends on oxygenate molecular structure.

Stoner and Litzinger [7] also concluded that the molecular structure of oxygenates plays a role in the formation of soot. The focus of their study was to determine how the structure and boiling point of oxygenates affect the emissions of NOx and soot. They performed engine tests on DEM, DBM, diglyme, triglyme, and tetraglyme blended with a base DF-2

to give 2 wt % oxygen. DEM and DBM are di-esters and the glymes are poly-ethers. The glyme series was investigated to determine the effect of oxygenate boiling on emissions.

The test engine was an optically accessible 2-stroke, direct injection single cylinder engine diesel built on a Waukesha/CFR crankcase. The compression ratio, 14, was relatively low for the engine volume, 612 cm<sup>3</sup>, which is more typical of a high-speed diesel engine. The injection pressure was not given in the paper, but was probably about 5,000 psi.

The engine was operated in a skip fire mode to retain temperatures and preserve optical access. The start of combustion was carefully controlled and ignition delays were noted. There was no EGR. Laser light extinction was used to measure time resolved, in-cylinder soot concentrations and gaseous exhaust emissions were measured by conventional methods.

All of the oxygenates examined reduced peak soot during combustion, but the maleates, DEM and DBM, appeared to be most effective in that they also reduced emissions of NOx. NOx was reduced 8.5% by DBM and 5% by DEM. Diglyme and triglyme caused a 2% increase in NOx while tetraglyme lowered NOx by about 2.5%. DEM, DBM and diglyme each reduced peak soot by about 12%, but peak soot levels were only lowered by 6.5 and 5% respectively for higher boiling triglyme and tetraglyme. The reductions in NOx caused by DEM and DBM appeared contrary to reason in that these oxygenates caused an increase in the Ignition delay. Generally speaking, an increase in ignition delay enhances premixed combustion, which tends to increase NOx and lower soot formation.

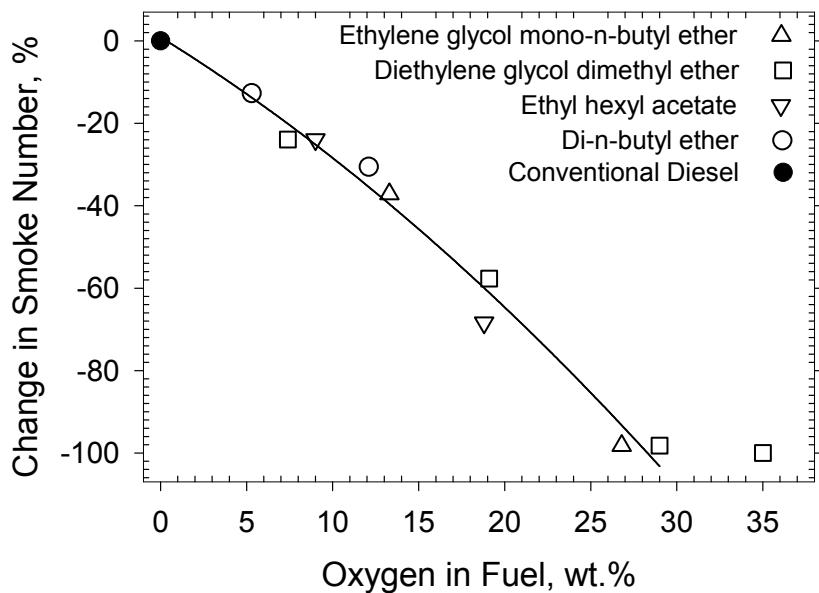
Litzinger and Stoner [8] performed a follow on study on DEM, DBM and diglyme in a 4 cylinder 1.9L direct injected Volkswagen turbo diesel. They used the same base DF-2 as in the previous study and added oxygenates in amounts to achieve 2 wt % oxygen in the blended test fuels. Performance and emissions tests were performed steady state at 6 operating conditions. Exhaust gases were sampled from a dilution tunnel and measured by conventional methods. In addition to total PM, the measurements included the volatile organic fraction, VOF, and the soluble organic fraction, SOF, of the PM. They determined soot formed during combustion by subtracting the SOF from the total PM.

At medium to low power, all of the oxygenated fuel blends yielded less soot than the base DF-2. The order of soot reduction at medium to low power was DBM > DEM > diglyme. At high power conditions, DEM and diglyme equally produced substantially less soot than the base DF-2, but, of great surprise, DBM produced as much or more soot than the base DF-2. The gaseous emissions of NOx, CO and HC were essentially the same for all the test fuels including the base DF-2. If anything, the composite NOx emissions from the DEM and DBM blends appeared to be slightly higher than that of the diglyme blend. In other words, just the opposite result from what Stoner and Litzinger [7] observed for NOx emissions in their previous study with the research engine.

Litzinger and Stoner hypothesize that oxygenates tend to form CO prematurely in the reaction zone. They propose that CO reacts with free radicals such as H, CH<sub>3</sub> and HO<sub>2</sub> to interfere with the precursor reactions that lead to soot formation. Since they are still developing this mechanism, they are not yet clear on the details of how the CO reactions inhibit the formation of soot.

Miyamoto et al. [9, 10] investigated the effects of several oxygenates on emission from a 4 stroke direct injected single cylinder engine. The engine had a compression ratio of 16.3 and stroke volume of 1007 cm<sup>3</sup>. The tests were conducted at a steady state mode (1320 rpm & 0.75 Mpa BMEP). Some of the oxygenates were blended with a base DF-2 and some were run in the engine in their pure form. The objective was to test several oxygenates for their ability to improve exhaust emissions from diesel engines.

They found that when the oxygen content of the fuel was raised to the 25 to 30% level, the smoke emissions were reduced to about 2% of what is typically observed for conventional diesel fuel. Figure 2 shows percent change in Bosch smoke number for several pure oxygenates and oxygenate-diesel blended fuels relative to a conventional diesel fuel. It is seen that the smoke emissions correlate with the oxygen content of the fuel and seem to be relatively independent of oxygenate molecular structure. However, it is important to note that while Bosch smoke number correlates with total exhaust PM, it does not necessarily represent soot formed in-cylinder.



**Figure 2. Smoke Emissions from Diesel Engines Operating on Oxygenated Fuels**  
(Miyamoto et al., Ref. 10)

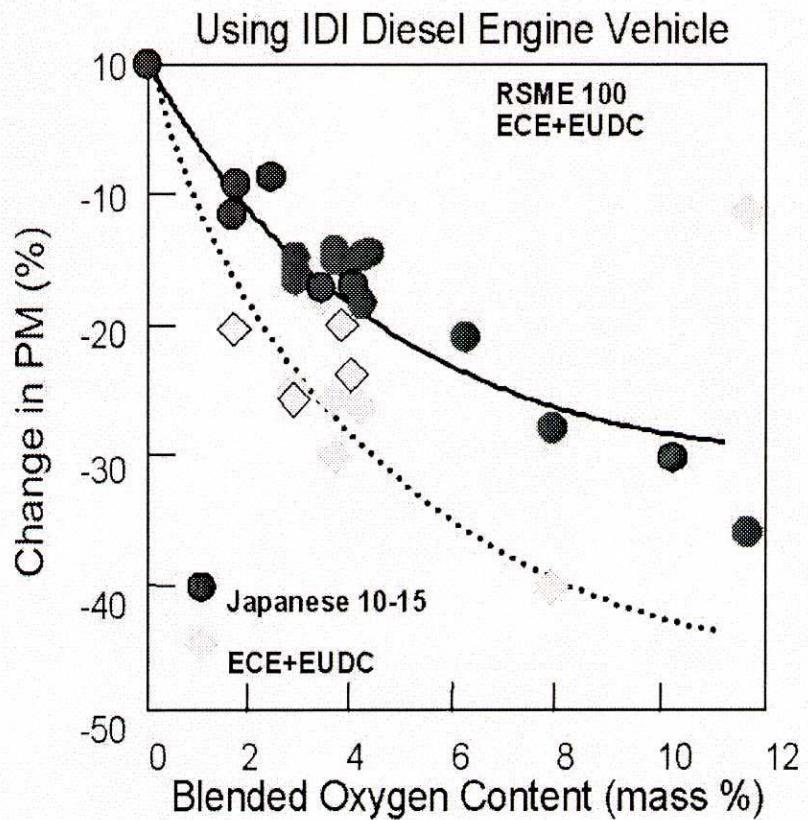
Tsurtni et al. [11] investigated the effects of aromatic content, distillation range – T90, cetane number & cetane improvers, and oxygenates on exhaust emissions from a 2.0L Toyota Corolla IDI with EGR and a 4.0L DI engine without EGR. The emissions in the 2.0L IDI engine were determined for the Japanese 10-15 and the ECE-EUDC transient test cycles. No exhaust after treatment was used on either engine. Engine details such as piston bowl shape and injection pressure were not given.

The pure hydrocarbon test fuels included a base fuel with a normal boiling range (IBP-EP) and three narrower cuts of the same, i.e., IBP-T80, T20-T80, and T20-T100. Additional blends were made with the heavy end enriched with di- and tri-cyclic aromatics. Oxygenates included 1GM, 2GM, 3GM, 4GM, DPE, MTBE, ENB, ETB, LBE, PME and RSME, which were blended in various proportions with the base fuel. RSME was tested in its pure form.

They found that lowering T90 reduced PM emissions in both the IDI and DI engines. The effect was much more pronounced in medium load than high load conditions. It seemed that the PM reduction was caused by a combined effect of decreasing the back end volatility and the poly-cyclic aromatics. Cetane improver tended to reduce PM emissions in fuels with lower cetane number (< 45) in the IDI engine but had no effect in the DI engine. Cetane improver had no effect on NOx emissions in either engine.

Of all the properties examined, oxygenates caused the greatest reduction in PM, but had little effect on NOx emissions. PM emissions varied with the test cycle. The PM reduction with respect to oxygen content shown in Figure 3 was more pronounced in the ECE-EUDC test cycle than the Japanese 10-15 test cycle. Oxygenates had a greater effect under mid-load than high load operating conditions in the 4.0L DI engine. It is interesting note the anomalous data point for the RSME bio-diesel fuel in Figure 3. The RSME fuel behaved as expected in the Japanese 10-15 test cycle, but showed a very meager PM reduction in the ECE-EUDC test cycle. The authors attribute the effect to the narrow and relatively high boiling range of the RSME fuel. However, the authors did not present a strong argument for why the PM reduction was so vastly different between the two test cycles. The results in Figure 3 show the PM reduction to be largely dependent on the oxygen content of the fuel. There is some scatter in the data that could be attributed to the effect of oxygenate molecular structure, but it is not discussed in the paper.

Uchida and Akasaka [12] tested blends of oxygenates TPE and SME with some light low-aromatic fuels and a commercial Japanese diesel fuel. The light low-aromatic fuels were also tested separately and compared with the commercial Japanese diesel fuel, which was the baseline fuel for all of the tests. The tests were performed in a commercial Japanese 1994 direct injection 6-cylinder, 8L turbodiesel with intercooler, which was compliant with 1994 Japanese emissions regulations. The Japanese 13-mode transient cycle test was used to evaluate the test fuels.



**Figure 3. Oxygen Impacts on Particulate emissions using the Japanese 10-15 and the ECE+EUDC Test Cycles (Tsurutani, et. al.)**

They found that light Diesel, including kerosene, decreased NO<sub>x</sub> and PM but increased HC and CO. The light paraffinic fuels reduced NO<sub>x</sub>, PM, HC and CO. A blend of 25 Vol.% TPE in the base fuel to give an oxygen content of about 8 wt.% reduced PM emissions by 38%. The SME oxygenate reduced PM similarly in proportion to the weight percent of oxygen in the fuel blend. It was found that SOF was significantly less in fuels with reduced aromatics. The SOF in the PM formed from the oxygenated fuels was greater than that of any of the hydrocarbon fuels. As a result, the oxygenated fuels produced substantially less dry PM or in-cylinder soot than the hydrocarbon based fuels.

Akasaka et al. [13] studied DMA and blends of DMA in a commercial DF-2. The fuels were tested in two single cylinder engines, an AVL 1357 cm<sup>3</sup> DI engine with a

compression ratio of 16 and an OSKA-D 624 cm<sup>3</sup> DI engine with compression ratio of 18. The latter was designed with impingement diffusion combustion, i.e., atomization was accomplished by impingement of the fuel jet on a flat node in the piston bowl. The OSKA-D engine had re-entrant lips on the piston bowl rim, but there were none on the bowl rim of the AVL engine. PM emissions were measured with a Bosch smoke meter.

Neat DMA burned smoke-free in the OSKA-D engine, while in the AVL engine, the exhaust smoke was very detectable, but much less than that from the commercial DF-2. The smoke emissions from DF-2 burned in the OSKA-D engine were lower than those from DF-2 which were burned in the AVL engine, but the difference was proportionately less than that for neat DMA. The NOx emission from DMA was much less than that from DF-2 in the OSKA-D engine, but was essentially the same for both fuels in the AVL engine. There was no discussion as to whether it was the re-entrant lips or the fuel jet impingement in the OSKA-D engine that improved the emissions. In blends of DMA in DF-2, DMA had no beneficial effect on smoke emissions until its concentration exceeded 50 Vol.%. They concluded that DMA would not be an appropriate blending agent for reducing smoke emissions.

Akasaka et al. [14] tested two alcohols, a carbonate, an ether and two glycol ethers blended with a commercial DF-2. The fuels were blended with oxygen-to-carbon ratios up to 0.1. Cetane improver was added to some of the blends to compensate for decreases in cetane number caused by oxygenates such as alcohols and carbonates, which tend to increase ignition delay. The actual chemical names of oxygenates used in the study were not disclosed in the paper. Steady-state tests were performed in single-cylinder DI and IDI engines and full-scale engine tests were performed in a transient-dyno facility on two commercial engines, which were compliant with 1989 Japanese emissions regulations.

The steady-state single cylinder tests were conducted with fuels having different O to C ratios, and the commercial engines were run on fuel blends with O to C ratios of 0.1 using the Japanese 13-mode transient test schedule. It was found that oxygenates reduced PM to an extent that mainly depended on the O to C ratio. However, there were some

instances where the PM reduction varied with the type of oxygenate used. When cetane improver was added to oxygenate DF-2 blends, there were reductions in HC, CO and PM. The NO<sub>x</sub> emissions were relatively independent of changes in fuel composition.

Akasaka et al. [15] tested SME and TPE blended with a low sulfur (300 ppm) DF-2 base fuel in a 8L direct injection 6-cylinder turbo diesel with intercooler. The engine met Japanese emissions regulations. The tests were conducted according to the transient D-13 mode test, which is used to evaluate heavy-duty DI diesel engines in Japan.

The emissions from blends of SME in DF-2 were lower in HC and PM, slightly higher in NO<sub>x</sub>, and about the same CO as the base fuel. On the basis of oxygen content, SME reduced PM emissions about 4 % and TPE about 6% for each 1 wt .% oxygen in the fuel. The SOF was higher in the PM produced by the oxygenated fuels. The PM from the SME blends was higher than that from the TPE blend. The results indicate that there may be a molecular structure effect, but when boil range and SOF are taken into account, it appears that on the basis of oxygen content, SME and TPE are equally effective in inhibiting the formation of soot.

Liotta and Montavio [16] tested aromatic and aliphatic alcohols, glycol ethers such as 2GM and SME in an 11.1L 6-cylinder 90 DDC series 60 diesel engine equipped with electronic unit injectors. Oxygenates were blended up to 5 vol. % in two stock baseline diesel fuels. One DF-2 was low sulfur with medium aromatics and the other was low sulfur with low aromatics. The base fuels varied significantly in density and cetane number. The tests were performed in accordance with the transient FTP HD test cycle. There was no mention of EGR use in the test procedure.

The gross observation was that oxygenates reduced PM emissions in proportion to the oxygen content of the fuel. However, some oxygenates appeared to be more effective at reducing PM emissions than others did. For an oxygen content of 2 wt.%, the reduction in PM emissions among the oxygenates tested ranged from 12 to 18%. It was noted that

ether bound oxygen seemed to be more effective than alcohol bound oxygen. Addition of cetane improver to the fuel blends tended to decrease emissions further.

Tamanouchi et al. [17] investigated the effects of increasing T90 by adding polycyclic aromatics, and adding 10 Vol.% of 2GM and a n-C<sub>14</sub> paraffin to a conventional DF-2 base fuel on exhaust emissions. The tests were performed in three heavy-duty diesel engine-dyno setups and one light-duty engine-vehicle system. Two engines were compliant with 1991 Japanese emissions requirements and one was compliant with 99 Japanese emissions requirements. The IDI engine in the vehicle complied with 93 Japanese emissions standards. The engine tests were conducted according to the Japanese 13-mode HD steady-state test cycle while the vehicle was subjected to the transient mode test. They found that the 10 Vol.% 2GM blend produced significantly less PM than the 10 Vol.% n-C<sub>14</sub> blend. PM went up when polycyclic aromatics were added to raise T90. The oxidation catalyst removed most of the SOF from the PM. The 2GM blend was particularly effective in reducing in-cylinder soot, so it was quite effective in lowering PM emissions when used in combination with the oxidation catalyst. The results were similar for both heavy and light duty engines.

Beatrice et al. [18] tested blends of 10, 20, and 30 Vol.% diglyme in a finished summer grade low sulfur (18 ppm) diesel fuel, FSG, in an intercooled Fiat M724 1.9L JTD Turbodiesel equipped with an exhaust oxidation catalyst. Tests were conducted at 3 modes, a low-speed low-medium load (1500 rpm, 3 bar BMEP), one representative of the European test procedure for exhaust emissions (2000 rpm, 2bar BMEP), and a low speed high load condition (2000 rpm, 6 bar BMEP). The latter was chosen to evaluate the effect of oxygen content on soot production. To gain complete electronic control of the engine, the ECU was replaced by a customized ECU coupled with an emulator memory unit.

Exhaust emissions were measured before and after the oxidation catalyst. Smoke number was measured with an AVL 415 smoke meter. PM mass was not measured. Table 2 shows that the diglyme-FSG blends gave significant reductions in all the emissions.

**Table 2. Effect of Diglyme on Emissions from FSG Low Sulfur Diesel, (2000 rpm, 2 bar BMEP)**

Test Fuel	Percent Reduction THC	Percent Reduction CO	Percent Reduction NOx	Percent Reduction Smoke
FSG	---	---	---	---
FSG + 10 Vol.% Diglyme	29	26	5	11
FSG + 20 Vol.% Diglyme	24	36	8	48
FSG + 30 Vol.% Diglyme	33	28.5	8	57

It was noted in the paper that because of the substantial reduction in smoke, the EURO III emissions standard could be achieved with the fuel blends containing 20 and 30 Vol.% diglyme.

Ullman, et. al. [19] tested 1GM and 2GM blended with DF-2 in a 1994 prototype DDC Series 60 heavy-duty diesel engine. The fuel blends contained up to 4wt.% oxygen. Spreen, et. al. [20] performed a similar study on 1GM and 2GM in a 1994 Navistar DTA466 heavy-duty diesel engine designed to meet 1994 emission standards using a catalytic converter. The tests showed that oxygenates reduced PM emissions by 6 to 7 % for every 1wt. % oxygen in the fuel. The effects of the glymes on the HC and NOx emissions varied with the calibration used. There was no mention of any difference between the effects of 1GM and 2GM. It appeared that the reductions in PM emissions depended only on the oxygen content of the fuel.

### 3.0 FUEL PROPERTY EFFECTS ON PM

In the work cited above, it was shown that the tendency to soot decreases as oxygen content of the fuel increases. However, no attempt was made to correlate fuel properties such as H to C ratio, T90, and viscosity with PM emissions in diesel engines. There have been several studies on the effects of fuel properties on PM emissions from hydrocarbon based fuels [21]. These studies have shown that reductions in sulfur, density, distillation temperature and aromatic content (especially multi-ring aromatics) lower PM emissions. However, Nkakita, et. al. [21] conclude that the chemical structure of the fuel also plays an important role in the formation of soot in diesel engine combustion.

Nkakita et al. [21] tested three fuels, namely, “Base, Improved, and Class-1” in 2 single cylinder engines of similar displacement and compression ratio. One engine, which had optical access, was used to investigate the in-cylinder combustion process, while the other was used to evaluate exhaust emissions. “Base” was an average market fuel in Japan with 21.9% aromatics. “Improved” was a low emissions fuel with fewer aromatics and a lower distillation temperature than “Base.” “Class-1” was a Swedish low-sulfur fuel with much less aromatics, a lower boiling point distribution and a lower density than “Improved.” Improved and Class-1 had similar hydrogen contents, which were higher than that of the “Base” fuel.

Both Improved and Class-1 had substantially lower PM emissions than “Base,” but of some surprise, the PM emissions from “Improved” were significantly less than from Class-1. The results of Nkakita et al. suggested that the relatively high concentrations of naphthenes and branched paraffins in Class-1 were responsible for the higher than expected PM emissions. To further substantiate their theory, they perform pyrolysis and shock tube studies, which showed that soot precursors such as benzene, toluene, acetylene and propadiene were more abundant in the high temperature decomposition of the Class-1 fuel [22]. They concluded that branch paraffins such as iso-octane should soot more than normal octane and cyclohexane should soot more than 1-hexene.

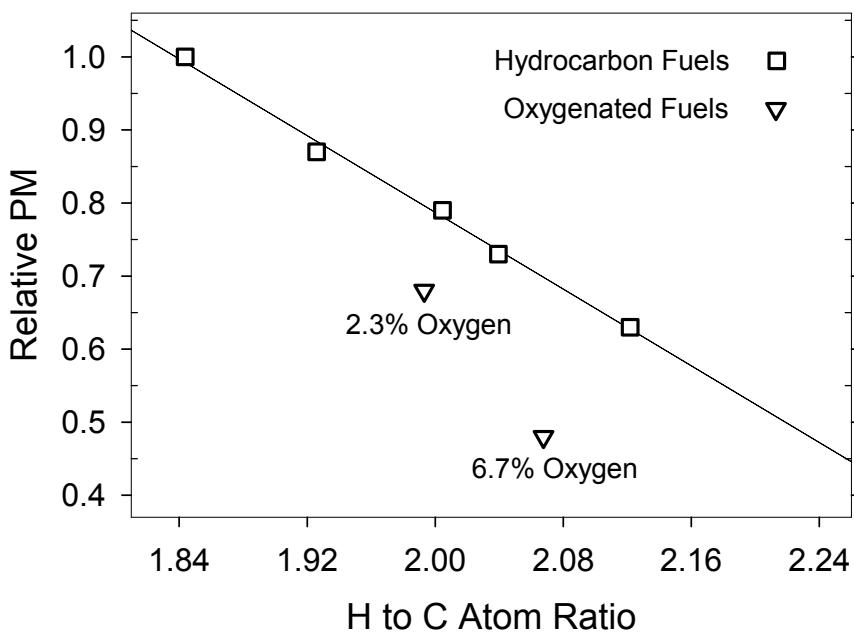
Takahashi and Glassman [23] investigated the sooting tendencies of several pure hydrocarbons including straight chain paraffins, branched paraffins, naphthenes, and aromatics in premixed flames. They measured the effect of flame temperature on the soot inception equivalence ratio, i.e., equivalence ratio at which soot incandescence begins to appear in the flame. They concluded that the structure of the fuel molecule, whether straight, branched or cyclic, does not affect the sooting tendency. Instead, they conclude that gross compositional properties including the H to C ratio and the number of C-C bonds in the molecule determine the sooting tendency. This also agrees with studies in gas turbine combustors [5], which show that sooting tendency is largely a function of H to C ratio.

Sirman, et. al. [24] tested six alternative fuels in an electronically controlled 2.2L DI Mercedes turbodiesel engine. Triplicate 13-mode, steady-state test sequences were performed for each fuel, as well as an ASTM D975 low sulfur DF-2 control fuel, which served as the baseline. Emissions measurements included HC, CO, NOx and PM. Total PM levels were determined gravimetrically by collecting particulate matter on a set of 90 mm Pallflex filters. The alternative fuels included the California Reference fuel, a low sulfur diesel, a Fischer-Tropsch diesel, and three blends: 20% Fischer-Tropsch/80% low-sulfur diesel, 20% biodiesel/80% low-sulfur diesel, and 15%DMM/85% low-sulfur diesel. The low-sulfur diesel was comparable to the Swedish, Class-1, urban diesel fuel used in the study of Nkakita et al. [21,22].

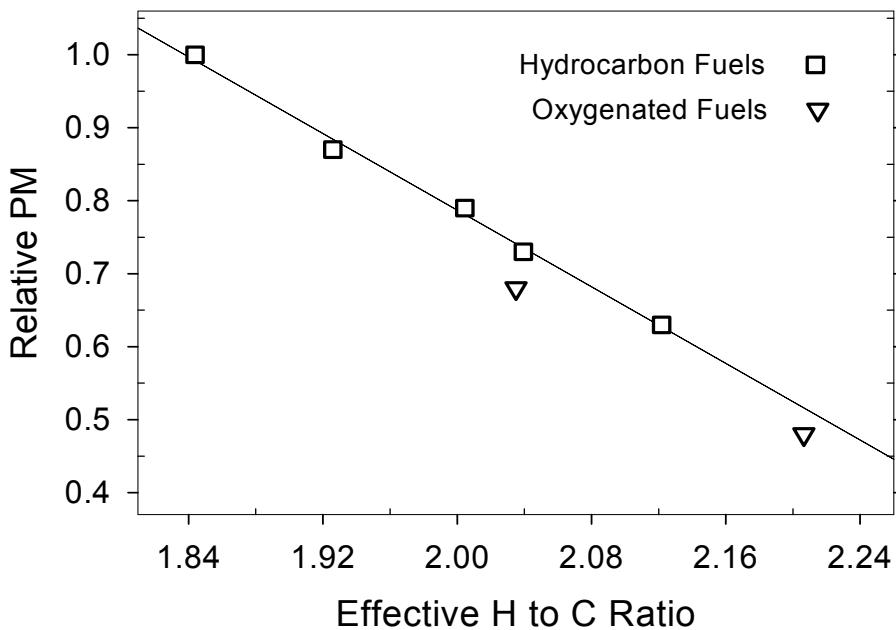
Sirman et al. found that the 15%DMM/85% low-sulfur blend containing 6.7% oxygen gave the greatest reduction in PM relative to the baseline DF-2. The composite average reduction in PM for the 13 modes was 52%. The Fischer-Tropsch diesel came in second with a 37% reduction in PM. Figure 3 shows that the PM emissions from the hydrocarbon fuels correlates favorably with the H to C ratio. The data in the figure are composite averages normalized relative to the baseline DF-2. The effect of oxygen in the fuels is shown by how far the data points for the oxygenated fuels fall below the line. In Figure 4, PM from the oxygenated fuels does not correlate with the H to C ratio. However, if it is considered that the carbon atoms tied up with oxygen atoms in the fuel do not participate in soot formation, the effective H to C ratio of a fuel containing oxygen may be expressed as

$$[\text{H/C}]_{\text{Effective}} = \text{H}/[\text{C-O}]$$

where H, C, and O are the relative numbers of atoms in the fuel. Figure 5 shows the correlation of the PM data with the effective H to C ratio. Note that the least-squares fit of the data does not include the oxygenated fuels. When the effective H to C ratio is used, the oxygenated fuels appear to correlate with H to C ratio in the same way as pure hydrocarbon fuels. This implies that the mechanism of soot formation in oxygenated fuels is the same as that in pure hydrocarbons. In other words, the only difference between oxygenated fuels and pure hydrocarbon fuels is that the carbon bonded to oxygen does not participate in the formation of soot.



**Figure 4. Correlation of “PM Exhaust Emissions” with the “Hydrogen to Carbon Ratios” of the Test Fuels. Composite Emissions Data from a 13 Mode Test in a 2.2 L Mercedes Turbodiesel.**



**Figure 5. Correlation of “PM Exhaust Emissions” with the “Effective Hydrogen to Carbon Ratio” of the Test Fuels. Composite Emissions Data from a 13 Mode Test in a 2.2 L Mercedes Turbodiesel.**

### **3.1 Conclusions**

- The cited references all report a correlation between fuel oxygen content and PM emissions somewhat irrespective of the chemical nature of the oxygen-containing species. The studies indicated that an oxygen content of at least 7% in the fuel would be required to produce a 50% reduction in PM.
- In some cases NO<sub>x</sub> effects are reported, and these are typically small and are usually explainable on the basis of the injection timing and fuel properties such as cetane number, which effect the extent of the premixed burn.
- Few of the test engines cited in the literature use state of the art fuel injection and combustion system technology. In the studies that revealed engine details, injection pressures were relatively low and nozzle holes were larger and fewer in number than in a modern high-speed DI (HSDI) diesel engines. Modern HSDI engines have re-entrant lips on the piston bowl rim to make squish more effective and improve fuel air mixing. In several of the studies cited, the engines did not have this feature. Since fuel effects were the main focus of the studies, it appeared that little attention was given to engine details such as the number and sizes of injector holes, injection pressure, piston-bowl and nozzle geometry, which inexorably affect the combustion processes related to exhaust emissions.
- While it is difficult to know, in absolute terms, the PM or soot emissions from some of the studies appeared to be high by modern standards. Hence, the effect of fuel chemistry may have been exaggerated relative to that expected if the same fuel studies were conducted in modern HSDI engines.

- In most of the studies, the H to C ratio, which is known to correlate with soot formation, was not reported. In one study that gave the hydrogen and carbon contents of the fuels, it was shown that the PM emissions from a light duty diesel correlated with the H to C ratio of the fuel. It was found that by excluding the carbon bonded to oxygen in the fuel, an effective H to C ratio could be calculated that correlated with the PM emissions from both pure hydrocarbon and oxygenated fuels.

#### **4.0 OXYGENATE SCREENING**

Several oxygenate candidates were revealed in the studies cited above, while others were proposed by the Ad Hoc group members of the project. As the project progressed, the oxygenate candidates shown in Table 3 grew to 71. Table 3 gives the oxygenate name, formula, oxygen content, volume percent of oxygenate required to give to 7 wt.% oxygen in an oxygenate-diesel fuel blend, density, flash point, and a pass/fail screening indication.

The initial criteria used to screen out the viable oxygenate candidates were 1) the amount of oxygenate added to diesel fuel to give 7 wt.% oxygen should not exceed 20 vol.%, 2) the flash point should not be less than 52°C, which is the specification for No. 2 diesel fuel, 3) oxygenate should be soluble in low aromatic diesel fuel at temperatures down to 6°C and tolerate at least 1000 ppm of water, and 4) oxygenate must not decompose into corrosive products. The data for criteria 1 and 2 were obtained from the literature (Table 3), whereas 3 and 4 had to be measured. Of the 71 oxygenate candidates in Table 3, 28 had flash points that were too low, and the oxygen contents were too low in three of the remaining 43.

**Table 3. Oxygenates Screening for Potential Use as Diesel Fuel Smoke Reducing Additives.**

Oxygenate	Chemical Structure	Oxygen Content Wt.%	Density Gr/mL @20C	Flash Point deg. C	Oxygenate Required For 7wt.% Oxygen In DF-2 Vol.%	Pass Or Fail
Tributyrin	C <sub>3</sub> H <sub>7</sub> (C=O)OCH[CH <sub>2</sub> O(C=O)C <sub>3</sub> H <sub>7</sub> ] <sub>2</sub>	31.7	1.0320	173	18.3	P
Di-butyl maleate	C <sub>4</sub> H <sub>9</sub> O(C=O)CH=CH(C=O)OC <sub>4</sub> H <sub>9</sub>	28.0	0.9880	> 110	21.6	P*
Triethyl citrate	HOC(O(C=O)C <sub>2</sub> H <sub>5</sub> )[CH <sub>2</sub> (C=O)OC <sub>2</sub> H <sub>5</sub> ] <sub>2</sub>	40.5	1.1370	>110	13.1	P
1,1,3,3-Tetraethoxypropane	[C <sub>2</sub> H <sub>5</sub> O] <sub>2</sub> CHCH <sub>2</sub> CH[OC <sub>2</sub> H <sub>5</sub> ] <sub>2</sub>	29.0	0.9190	42	22.1	P*
Tripropylene glycol monomethyl ether	CH <sub>3</sub> [OC <sub>3</sub> H <sub>6</sub> ] <sub>3</sub> OH	31.0	0.9680	> 110	19.8	P
Tetraethylene glycol dimethyl ether (tetraglyme)	CH <sub>3</sub> O[C <sub>2</sub> H <sub>4</sub> O] <sub>4</sub> CH <sub>3</sub>	36.0	1.0090	140	16.4	P
Diethyl adipate	C <sub>2</sub> H <sub>5</sub> O(C=O)[CH <sub>2</sub> ] <sub>4</sub> (C=O)OC <sub>2</sub> H <sub>5</sub>	31.6	1.0090	110	18.8	P
Dibutoxy methane (Butylal)	C <sub>4</sub> H <sub>9</sub> OCH <sub>2</sub> OC <sub>4</sub> H <sub>9</sub>	20.0	0.8354	62	34.6	F
Diethylene glycol ethyl ether acetate	CH <sub>3</sub> (C=O)OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub>	36.3	1.0120	107	16.2	P
Diethylene glycol diacetate	CH <sub>3</sub> (C=O)OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> O(C=O)CH <sub>3</sub>	42.1	1.1159	135	12.8	P
Diethyl maleate	C <sub>2</sub> H <sub>5</sub> O(C=O)CH=CH(C=O)OC <sub>2</sub> H <sub>5</sub>	37.2	1.0640	121	15.2	P
Triethylene glycol mono-ethyl ether	C <sub>2</sub> H <sub>5</sub> O CH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OH	35.9	1.0200	135	16.3	P
Triethylene glycol dimethyl ether (Triglyme)	CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	35.9	0.9860	111	16.8	P
2-Butoxyethyl acetate	CH <sub>3</sub> C(O)OCH <sub>2</sub> CH <sub>2</sub> OC <sub>4</sub> H <sub>9</sub>	30.0	0.9420	76	21.0	P*
Diethyl succinate	C <sub>2</sub> H <sub>5</sub> O(C=O)CH <sub>2</sub> CH <sub>2</sub> (C=O)OC <sub>2</sub> H <sub>5</sub>	36.7	1.0402	90	15.7	P
Dimethyl adipate	CH <sub>3</sub> O(C=O)[CH <sub>2</sub> ] <sub>4</sub> (C=O)OCH <sub>3</sub>	36.7	1.0630	107	15.4	P
2-Ethoxy ethyl ether	[C <sub>2</sub> H <sub>5</sub> OCH <sub>2</sub> CH <sub>2</sub> ] <sub>2</sub> O	29.6	0.9090	54	21.8	P*
Butyl lactate	CH <sub>3</sub> CH(OH)(C=O)OC <sub>4</sub> H <sub>9</sub>	32.8	0.9840	69	18.4	P
Dipropylene glycol mono-methyl ether	CH <sub>3</sub> OC <sub>3</sub> H <sub>6</sub> OC <sub>3</sub> H <sub>6</sub> OH	32.4	0.9380	74	19.4	P
1,1,3,3 – Tetramethoxy propane	[CH <sub>3</sub> O] <sub>2</sub> CHCH <sub>2</sub> CH[OCH <sub>3</sub> ] <sub>2</sub>	39.0	0.9970	54	15.3	P
Di-propoxy methane, n-Propylal	C <sub>3</sub> H <sub>7</sub> OCH <sub>2</sub> OC <sub>3</sub> H <sub>7</sub>	24.2	0.8338	26	28.6	F
Di-isopropoxy methane, Isopropylal	CH[CH <sub>3</sub> ] <sub>2</sub> OCH <sub>2</sub> OCH[CH <sub>3</sub> ] <sub>2</sub>	24.2	0.8156	9	29.0	F
Triethylene glycol monomethyl ether	CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OH	39.0	1.0260	118	14.9	P
2,5,7,10-Tetra-oxa-undecane (TOU)	CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	39.0	0.9898	88	15.4	P

**Table 3. Oxygenates Screening for Potential Use as Diesel Fuel Smoke Reducing Additives.**

Oxygenate	Chemical Structure	Oxygen Content Wt.%	Density Gr/mL @20C	Flash Point deg. C	Oxygenate Required For 7wt.% Oxygen In DF-2 Vol.%	Pass Or Fail
3-Methoxybutyl acetate (Butoxyl)	CH <sub>3</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH[CH <sub>3</sub> ]OCH <sub>3</sub>	32.8	1.0000	77	18.2	P
Diacetin	HOCH[CH <sub>2</sub> O(C=O)CH <sub>3</sub> ] <sub>2</sub>	45.4	1.1700	110	11.3	P
Diethyl malonate	C <sub>2</sub> H <sub>5</sub> O(C=O)CH <sub>2</sub> (C=O)OC <sub>2</sub> H <sub>5</sub>	40.0	1.0550	99	14.2	P
Dipropyl carbonate	C <sub>3</sub> H <sub>7</sub> O[C=O]OC <sub>3</sub> H <sub>7</sub>	32.8	0.9411	55	19.1	P
Isopropyl lactate	CH <sub>3</sub> CH[OH][C=O]OC <sub>3</sub> H <sub>7</sub>	36.3	0.9880	57	16.5	P
2-butoxy ethanol	C <sub>4</sub> H <sub>9</sub> OCH <sub>2</sub> CH <sub>2</sub> OH	27.1	0.9030	60	24.0	F
Dimethyl maleate	CH <sub>3</sub> O[C=O]CH=CH[C=O]OCH <sub>3</sub>	44.4	1.1520	113	11.8	P
Ethylene glycol diacetate	CH <sub>3</sub> [C=O]OCH <sub>2</sub> CH <sub>2</sub> O[C=O]CH <sub>3</sub>	43.8	1.1280	96	12.2	P
2,4,7,9-Tetra-oxa-decane (TOD)	CH <sub>3</sub> OCH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> OCH <sub>3</sub>	42.6	1.0050	68	13.8	P
Diglyme	CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	35.8	0.9451	67	17.4	P
Diethylene glycol monoethyl ether	CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OH	35.8	0.9700	96	17.1	P
Ethylene glycol monoethyl ether acetate	CH <sub>3</sub> [C=O]OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> H <sub>5</sub>	36.3	0.9748	52	16.7	P
Ethyl aceto acetate (acetoacetic ester)	CH <sub>3</sub> [C=O]CH <sub>2</sub> [C=O]OCH <sub>2</sub> CH <sub>3</sub>	36.9	1.0250	57	15.8	P
Diethoxy acetal	CH <sub>3</sub> CH[OCH <sub>2</sub> CH <sub>3</sub> ] <sub>2</sub>	27.1	0.8310	-20	25.6	F
Dimethyl Succinate	CH <sub>3</sub> O(C=O)CH <sub>2</sub> CH <sub>2</sub> (C=O)OCH <sub>3</sub>	43.8	1.1170	85	12.3	P
Tetramethoxy ortho carbonate	C[OCH <sub>3</sub> ] <sub>4</sub>	47.0	1.0230	60	12.3	P
Diethylene glycol monomethyl ether	CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OH	39.9	1.0100	96	14.7	P
2-Methoxyethyl acetate	CH <sub>3</sub> [C=O]OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	40.6	1.0070	43	14.5	P
Diethyl carbonate	CH <sub>3</sub> CH <sub>2</sub> O[C=O]OCH <sub>2</sub> CH <sub>3</sub>	40.6	0.9750	25	14.9	P*
Diethoxy methane, Ethylal, (DEM)	CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub>	30.7	0.8300	-7	22.6	F
Isopropyl acetate	CH <sub>3</sub> [C=O]OCH(CH <sub>3</sub> ) <sub>2</sub>	31.3	0.8737	2	21.3	F
Trimethyl acetic acid	C[CH <sub>3</sub> ] <sub>3</sub> [C=O]OH	31.3	0.8890	63	21.0	P*
Acetyl acetone	CH <sub>3</sub> [C=O]CH <sub>2</sub> [C=O]CH <sub>3</sub>	32.0	0.9753	41	19.1	F
Methyl tertiary butyl ether, (MTBE)	CH <sub>3</sub> C[CH <sub>3</sub> ] <sub>2</sub> OCH <sub>3</sub>	18.6	0.7580	-10	39.5	F
Dimethyl malonate	CH <sub>3</sub> O(C=O)CH <sub>2</sub> (C=O)OCH <sub>3</sub>	48.4	1.1560	90	10.7	P

**Table 3. Oxygenates Screening for Potential Use as Diesel Fuel Smoke Reducing Additives.**

Oxygenate	Chemical Structure	Oxygen Content Wt.%	Density Gr/mL @20C	Flash Point deg. C	Oxygenate Required For 7wt.% Oxygen In DF-2 Vol.%	Pass Or Fail
Tetrahydrofurfuryl alcohol	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CHOCH <sub>2</sub> OH	31.3	1.0543	83	18.3	P
Diethylene glycol	HOCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OH	45.2	1.1184	143	11.8	P
Trimethyl orthoformate	CH[OCH <sub>3</sub> ] <sub>3</sub>	45.2	0.9700	15	13.4	F
Dimethoxyethane (Glyme)	CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	35.5	0.8683	40	18.8	F
2-Ethoxy ethanol	CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OH	35.5	0.9300	54	17.8	P
Dimethylacetal (DMA)	CH <sub>3</sub> CH[OCH <sub>3</sub> ] <sub>2</sub>	35.5	0.8516	-20	19.1	F
Ethyl acetate	CH <sub>3</sub> [C=O]OCH <sub>2</sub> CH <sub>3</sub>	36.3	0.9020	7	17.8	F
1-Methoxy-2-propanol	CH <sub>3</sub> CH[OH]CH <sub>2</sub> OCH <sub>3</sub>	35.5	0.9220	33	17.9	F
Butanal	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CHO	22.2	0.8000	-11	32.1	F
T-Butanol	CH <sub>3</sub> C[CH <sub>3</sub> ] <sub>2</sub> OH	21.6	0.7860	4	33.4	F
I-Butanol	CH <sub>3</sub> CH[CH <sub>3</sub> ]CH <sub>2</sub> OH	21.6	0.8032	38	32.9	F
N-Butanol	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	21.6	0.8109	46	32.7	F
Trioxane	Cyclo-CH <sub>2</sub> OCH <sub>2</sub> OCH <sub>2</sub> O	53.3	1.1700	45	9.6	F
Dimethyl carbonate	CH <sub>3</sub> O[C=O]OCH <sub>3</sub>	53.3	1.0718	18	10.4	F
Methyl acetate	CH <sub>3</sub> [C=O]OCH <sub>3</sub>	43.2	0.9320	-9	14.5	F
Dimethoxymethane, Methylal (DMM)	CH <sub>3</sub> OCH <sub>2</sub> OCH <sub>3</sub>	42.1	0.8560	-28	16.1	F
Methoxy ethanol	CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OH	42.1	0.9663	43	14.5	F
Propanal	CH <sub>3</sub> CH <sub>2</sub> CHO	27.5	0.8050	-26	25.8	F
Dimethyl ether (DME)	CH <sub>3</sub> OCH <sub>3</sub>	34.7	0.6100	<-26	25.3	F
Acetaldehyde	CH <sub>3</sub> CHO	36.3	0.7880	<-26	19.9	F
Ethanol	CH <sub>3</sub> CH <sub>2</sub> OH	34.7	0.7940	16	20.7	F
Methanol	CH <sub>3</sub> OH	49.9	0.8130	11	14.1	F

Solubility tests were performed on the remaining oxygenate candidates. The candidates were tested for solubility in Fischer Tropsch diesel (FT) and Swedish Class-1 Low Sulfur diesel (SLS) reference fuels. FT diesel was mostly composed of paraffins while SLS diesel, which was prepared by hydrotreating a petroleum based middle distillate, contained a sizable fraction of naphthenes. Neither reference fuel contained more than 2% aromatics. Since aromatics in diesel fuel tend to increase the solubility of oxygenates, the FT and SLS fuels represented a worse case for solubility. Solubility tests were conducted by vigorously mixing 25mL of oxygenate with 50mL of diesel reference fuel and then centrifuging the mixture to achieve rapid separation of insoluble components. Tables 4 and 5 show the of solubility test results for oxygenates in the FT and SLS fuels respectively. Oxygenate solubility was measured in terms of the amount of phase separation that occurred. In other words, a phase separation of 25 mL in Tables 4 and 5 indicates that oxygenate is completely immiscible in the test fuel. Oxygenates that separated from the base DF-2 at room temperature were ruled out as viable candidates. If there was no separation at room temperature, the solubility test was repeated at 6°C. If the oxygenate remained miscible at 6°C, a water tolerance test was performed. For water tolerance, the above test was conducted at room temperature with water added in the amounts of 0.1, 0.2, 0.67, 1.33, and 2.0 percent.

The criteria for acceptance was that the oxygenate-diesel fuel mix had to tolerate at least 0.2% water. In instances where water did not cause separation, the water was either absorbed into the fuel or remained as a separate phase. There were as many as three phases in some cases; one of the oxygenate-diesel fuel mix, one of insoluble oxygenate, and one of water. It was understood that there was some intermingling of the components among the various phases, however, this was beyond the scope of the project and was not investigated.

**Table 4. Test for Solubility of Oxygenates in Fischer Tropsch Diesel Fuel**

Status	Oxygenate	Separation 23 °C ML	Separation 5 °C mL	Separation 0.1 vol.% Water	Separation 0.2 vol.% Water	Separation 0.67 vol.% Water	Separation 1.33 Vol.% Water	Separation 2.0 Vol.% Water
A	Tributyrin	0	0	0/0.1	0/0.2	0 / 0.5	0 / 1	0 / 1.5
A	Di-butyl maleate	0	0	0/0.1	0/0.2	0 / 0.5	0 / 1	0 / 1.5
D	Triethyl Citrate	25	NA*	-----	-----	-----	-----	-----
B	Tri-propylene glycol monomethyl ether	0	0	0.3	0.35	25 / 0	-----	-----
D	Tetra-ethylene glycol di-methyl ether, Tetraglyme	21	NA	-----	-----	-----	-----	-----
D	Diethylene glycol ethyl ether acetate	25	NA	-----	-----	-----	-----	-----
D	Diethyl Adipate	0	16	-----	-----	0 / 0.5	0 / 1	1 / 1.5
D	Diethylene glycol diacetate	25	NA	-----	-----	-----	-----	-----
D	Triethylene glycol mono-ethyl ether	27	NA	-----	-----	-----	-----	-----
D	Triethylene glycol dimethyl ether, Triglyme	14	NA	-----	-----	19 / 0	-----	-----
D	Diethyl Succinate	21	NA	-----	-----	-----	-----	-----
D	Dimethyl Adipate	25	NA	-----	-----	-----	-----	-----
A	2-Butoxyethyl acetate	0	0	0/0.1	0/0.2	0 / 0.5	0 / 1	0 / 1.5
D	Triethylene glycol monomethyl ether	25	NA	-----	-----	-----	-----	-----
D	Diethyl maleate	25	NA	-----	-----	-----	-----	-----
A	Butyl lactate	0	0	0.1	0/0.2	8 / 0	25 / 0	-----
D	Di-propylene glycol mono-methyl ether	0	20+	-----	-----	25 / 0	-----	-----
A	1,1,3,3 - Tetramethoxy propane	0	0	0/0.1	0.2	0 / 0.5	0 / 1.3, b	0 / 2.6, b
C	2,5,7,10-Tetra-oxa-undecane (TOU)	1	17	-----	-----	18 / 0	20 / 0	21 / 0
U	3-Methoxybutyl acetate (Butoxyl)	NA	NA	NA	NA	NA	NA	NA
A	Dipropyl Carbonate	0	0	NA	NA	NA	NA	NA
D	Diethyl malonate	20	NA	-----	-----	-----	-----	-----
D	Isopropyl lactate	23	NA	-----	-----	-----	-----	-----
D	Dimethyl maleate	25	NA	-----	-----	-----	-----	-----
A	2-butoxy ethanol	0	0	0	0	0 / 0	0 / 0	23 / 0
D	Ethylene Glycol Diacetate	25	NA	-----	-----	-----	-----	-----
C	2,4,7,9-Tetra-oxa-decane (TOD)	9	NA	-----	-----	12.0 / 0	13.0 / 0	14 / 0.4

**Table 4. Test for Solubility of Oxygenates in Fischer Tropsch Diesel Fuel**

Status	Oxygenate	Separation 23 °C mL	Separation 5 °C mL	Separation 0.1 vol.% Water	Separation 0.2 vol.% Water	Separation 0.67 vol.% Water	Separation 1.33 Vol.% Water	Separation 2.0 Vol.% Water
D	Diethylene glycol monoethyl ether	25	NA	-----	-----	-----	-----	-----
D	Dimethyl Succinate	27	NA	-----	-----	-----	-----	-----
D	2-Ethoxy ethyl acetate	0	10+	-----	-----	10	16 / 0.8	18.5 / 1.5
D	Ethyl Acetoacetate	25	NA	-----	-----	-----	-----	-----
D	Dimethyl malonate	27	NA	-----	-----	-----	-----	-----
A	Trimethyl acetic acid	0	NA	-----	-----	0 / 0.5	0 / 1	0 / 1.5
D	2-Methoxyethyl acetate	>20	>23	-----	-----	-----	-----	-----
A	Diethyl carbonate	0	0	0/0.1	0/0.2	0 / 0.5	0 / 1	0 / 1.5
D	Diethylene glycol monomethyl ether	25	NA	-----	-----	-----	-----	-----
D	Tetrahydrofurfuryl alcohol	25	NA	-----	-----	-----	-----	-----
D	2-Ethoxy ethanol	25	NA	-----	-----	-----	-----	-----
D	Diethylene glycol	30	NA	-----	-----	-----	-----	-----
D	1-Methoxy-2-Propanol	25	NA	-----	-----	-----	-----	-----
D	Dimethyl carbonate	25	NA	-----	-----	-----	-----	-----
A	Methylal (DMM)	0	0	0/0.1	0/0.2	0 / 0.5	0 / 1	0 / 1.5
Slash, /, Indicates a two-phase separation – “mL of Oxygenate on top/ mL of water on bottom,”								
B – Indicates that some oxygenate dissolved in water phase.								
A	Soluble in fuel and water does not cause oxygenate separation from fuel.							
B	Soluble in fuel, but water causes oxygenate separation from fuel.							
C	Soluble in fuel, but trace water causes oxygenate separation from fuel.							
D	Insoluble in Fuel							
NA = Not Applicable								

**Table 5. Test for Solubility of Oxygenates in Swedish Low Sulfur Diesel Fuel**

Status	Oxygenate	Separation @ 23 °C mL	Separation @ 5 °C mL	Separation 0.1 vol.% Water mL	Separation 0.2 vol.% Water mL	Separation 0.67 vol.% Water mL	Separation 1.33 Vol.% Water mL	Separation 2.0 Vol.% Water mL
A	Tributyrin	0	0	0/0.1	0/0.2	0/0.5	0/1.0	0/1.5
A	Di-butyl maleate	0	0	0/0.1	0/0.2	0/0.5	0/1.0	0/1.5
D	Triethyl Citrate	25	NA*	-----	-----	-----	-----	-----
A	1,1,3,3-TetraEthoxyPropane	0	0	NA	NA	NA	NA	NA
A	Tripropylene glycol monomethyl ether	0	0	0	0	20 / 0	27 / 0	NA
D	Tetraethylene glycol di-methyl ether, Tetraglyme	25	NA	-----	-----	-----	-----	-----
A	Diethyl Adipate	0	0	0/0.1	0/0.2	0/0.5	0/1.0	0/1.5
D	Diethylene glycol ethyl ether acetate	26	NA	-----	-----	-----	-----	-----
D	Diethylene glycol diacetate	25	NA	-----	-----	-----	-----	-----
D	Triethylene glycol mono-ethyl ether	30	NA	-----	-----	-----	-----	-----
C	Triethylene glycol dimethyl ether, Triglyme	0	16	-----	-----	20 / 0	25 / 0	-----
A	2-Butoxyethyl acetate	0	0	0/0.1	0/0.2	0/0.5	0/1.0	0/1.5
D	Diethyl maleate	25	NA	-----	-----	-----	-----	-----
D	Diethyl Succinate	21	NA	-----	-----	-----	-----	-----
D	Dimethyl Adipate	26	NA	-----	-----	-----	-----	-----
A	2-Ethoxy Ethyl Ether	0	0	0/0.1	0/0.2	NA	NA	NA
A	Butyl lactate	0	0	0	0	0 / 0.5	1.0 / 1	4.0 / 1
B	Di-propylene glycol mono-methyl ether	0	0	0	16+	23 / 0	28 / 0	-----
A	1,1,3,3 - Tetramethoxy propane	0	0	0/0.1	0/0.2	0 / 0.5	1.5 *b	2 *b
D	Triethylene glycol monomethyl ether	25	NA	-----	-----	-----	-----	-----
B	2,5,7,10-Tetra-oxa-undecane (TOU)	0	4	15	-----	2.7 / 0	10 / 0	18 / 0
U	3-Methoxybutyl acetate (Butoxyl)	NA	NA	-----	-----	-----	-----	-----
A	Dipropyl Carbonate	0	0	0/0.1	0/0.2	-----	-----	-----
D	Diethyl malonate	19	NA	-----	-----	-----	-----	-----
C	Isopropyl lactate	0	22	-----	-----	-----	-----	-----
A	2-butoxy ethanol	0	0	0	0	0 / 0	0 / 0	0 / 0

**Table 5. Test for Solubility of Oxygenates in Swedish Low Sulfur Diesel Fuel**

Status	Oxygenate	Separation @ 23 °C mL	Separation @ 5 °C mL	Separation 0.1 vol.% Water mL	Separation 0.2 vol.% Water mL	Separation 0.67 vol.% Water mL	Separation 1.33 Vol.% Water mL	Separation 2.0 Vol.% Water mL
D	Dimethyl maleate	25	NA	-----	-----	-----	-----	-----
D	Ethylene Glycol Diacetate	25	NA	-----	-----	-----	-----	-----
A	2,4,7,9-Tetra-oxa-decane (TOD)	0	0	0.2	7	13 / 0	9.5 / 1.5	6.5 / 3.5, b
D	Diethylene glycol monoethyl ether	25	NA	-----	-----	-----	-----	-----
A	2-Ethoxy ethyl acetate	0	0	0.125 / .075	0.20 / 0.10	0.5 / 0.5	0 / 1.3, b	0 / 2, b
D	Dimethyl Succinate	26	NA	-----	-----	-----	-----	-----
D	Ethyl Acetoacetate	25	NA	-----	-----	-----	-----	-----
D	Diethylene glycol monomethyl ether	25	NA	-----	-----	-----	-----	-----
D	Dimethyl malonate	30	NA	-----	-----	-----	-----	-----
A	Trimethyl acetic acid	0	0	0/0.1	0/0.2	0/0.5	0/1.0	0/1.5
D	2-Methoxyethyl acetate	20	NA	-----	-----	-----	-----	-----
A	Diethyl carbonate	0	0	0/0.1	0/0.2	0/0.5	0/1.0	0/1.5
D	Tetrahydrofurfuryl alcohol	25	NA	-----	-----	-----	-----	-----
D	Diethylene glycol	28	NA	-----	-----	-----	-----	-----
D	2-Ethoxy ethanol	25	NA	-----	-----	-----	-----	-----
C	1-Methoxy-2-Propanol	0	20	NA	NA	21	25	NA
D	Dimethyl carbonate	25	NA	-----	-----	-----	-----	-----
A	Methylal (DMM)	0	0	0/0.1	0/0.2	0/0.5	0/1.0	0/1.5

Slash, /, Indicates a two-phase separation – “mL of Oxygenate on top/ mL of water on bottom,”

b – Indicates that some oxygenate dissolved in water phase.

A Soluble in fuel and water does not cause oxygenate separation from fuel.

B Soluble in fuel, but water causes oxygenate separation from fuel.

C Soluble in fuel, but trace water causes oxygenate separation from fuel.

D Insoluble in Fuel

\*NA = Not Applicable

Inspection of Tables 4 and 5 shows that oxygenates were less soluble in FT than in SLS diesel fuel. Of the oxygenates tested, 10 out of 42 rated an “A” for solubility in FT diesel while 16 out of 44 rated an “A” solubility in SLS diesel fuel. Actually, just 40 of the oxygenate candidates from Table 3 qualified for solubility testing, but a few more were tested because they were marginal on flash point and oxygen content, and some were favored by the Ad Hoc committee for special benefits such as availability and low toxicity. Methylal (DMM) was included in the solubility test because its combustion and fuel related properties are well known [25], and it has been evaluated in several engine tests on diesel emissions. Because so few oxygenates were soluble in FT diesel, all oxygenates that passed the solubility test in SLS diesel were considered as viable candidates. One exception was Timethyl acetic acid, which passed the solubility tests, but was dropped from the study because it had a very bad odor.

Stability and the tendency to cause corrosion were determined by the NACE D 665 corrosion test. The D 665 test measures the degree of corrosion that develops on a steel spindle immersed in a mixture of 30mL of water and 300mL of the oxygenate-diesel fuel blend. The mixture is stirred and held at 60°C for 4 hours after which the spindle is removed and inspected for corrosion. The test fuels were prepared by blending oxygenate candidates with SLS diesel in amounts required to achieve an oxygen content of 7 wt.% in the fuel blend.

The results of the D 665 NACE corrosion test are given in Table 6. Corrosivity of the test fuel was rated by the amount of rust on the spindle. If there was no rust on the spindle, the fuel “passed” the test according to the specifications in the D 665 method. If there were fewer than 6 rust spots, the fuel was given an A-rating. The fuel was given a B-rating if less than half of the spindle was covered with rust, and a C-rating if more than half of the spindle was rusted. Since only the base fuel, SLS diesel, and 3 oxygenates, 2-Ethoxy ethyl ether, 1-Methoxy-2-propanol, and Diethyl adipate, “passed” the test, the Ad Hoc committee had to be more lenient in grading the test fuels. Hence, it was decided that ratings of A and B would be allowed to pass, but a C would fail.

**Table 6. Final Screening Results Including the NACE Corrosion Test**

Status	Oxygenate	Oxygen Wt. %	Vol.% of Oxygenate for a 7% Oxygen Diesel Blend	Flash Point °C	Solubility in DF-2	4 Hour NACE D 665 Test
A	Tributyrin	31.7	18.3	173	Excellent	Pass-B
A	Di-butyl maleate	28.0	21.6	110	Excellent	Pass-B
D	1,1,3,3-TetraEthoxyPropane	29.0	22.1	42	Excellent	Failed-C
A	Tri-propylene glycol monomethyl ether	31.0	19.8	> 110	Good	Pass-B
D	2-Butoxyethyl acetate	30.0	21.0	76	Excellent	Failed-C
A	2-Ethoxy Ethyl Ether	29.6	21.8	54	Excellent	Passed
D	Butyl lactate	32.8	18.4	69	Excellent	Failed-C
D	1,1,3,3 – Tetramethoxy propane	39.0	15.3	54	Excellent	Failed-C
D	Dipropyl Carbonate	32.8	19.1	55	Excellent	Failed-C
A	Di-propylene glycol mono-methyl ether	32.4	19.4	74	Good	Pass-B
A	2-butoxy ethanol	27.1	24.0	60	Excellent	Pass-B
A	2-Ethoxy ethyl acetate	36.3	16.7	52	Good	Pass-A
D	Diethyl carbonate	40.6	14.9	25	Excellent	Failed-C
C	1-Methoxy-2-Propanol	35.5	17.9	33	Acceptable	Passed
A	Diethyl Adipate	31.6	18.8	110	Good	Passed
B	2,4,7,9-Tetra-oxa-decane (TOD)	42.6	13.8	68	Acceptable	Pass-A
D	2,5,7,10-Tetra-oxa-undecane (TOU)	39.0	15.4	88	Marginal	Failed-C

Grading the NACE D665 Test

- Passed – No corrosion on the steel spindle
- Pass-A - "Light corrosion" - Less than 6 rust spots on spindle
- Pass-B - "Medium corrosion" - 6 or more rust spots - more than half of surface is rust free
- Failed-C - "Heavy corrosion" - most of the Spindle surface is rusted

Status Definitions

- A - Acceptable for blending with convention diesel fuel.
- B - Same as A, but not available in quantities required for engine testing.
- C - Unacceptable for blending with conventional diesel fuel because of low flash point.
- D - Unacceptable for blending with conventional diesel fuel.

Table 6 shows 8 oxygenates with an “A” rating, one with a “B” and one with a “C.” 2,4,7,9-Tetra-oxa-decane was given a “B” rating because it was not available in quantity required for an engine test. 1-Methoxy-2-Propanol was rated with a “C” because its flash point was below the required 52°C limit. However, 1-Methoxy-2-Propanol was retained as a candidate for engine testing because it was a member of an homologous series of mono-, di-, and tri-propylene glycol mono-methyl ethers, which would be used to determine the effect of boiling point on PM emissions.

## 5.0 ENGINE TESTING

Exhaust emissions and performance testing was conducted in the 2.2L DaimlerChrysler OM611 inter-cooled turbo-diesel equipped with a high pressure common rail fuel system, electronic fuel injectors and EGR. Emissions tests on the oxygenated test fuels were performed in triplicate at Mode 6 (2300 rpm & 4.2 bar BMEP). Emissions tests on the ALS base fuel were performed in triplicate at Modes 5, 6, 10 and 11 (Table 7). EGR was set at 15%, and the start of injection was adjusted for each fuel to achieve peak pressure at 7 °ATDC. The Bosch smoke number, total PM, total volatile fraction (TVF), NO<sub>x</sub>, CO, THC, CO<sub>2</sub>, and O<sub>2</sub> were measured. Dry PM, which is assumed to form during the combustion process, was calculated by subtracting the TVF from the total PM.

Table 7. Steady-State Test Points		
Mode	RPM	BMEP, bar
6	2300	4.2
5	2600	8.8
10	2000	2.0
11	1500	2.6

The oxygenate candidates eligible for engine testing were blended with alternative low sulfur diesel fuel, ALS, in the amounts required to achieve an oxygen content of 7 wt.%. The ALS base fuel was a petroleum product made sulfur free (< 2 ppm) and low aromatic (9 %) by hydro-treating a conventional diesel stock. The density, viscosity, surface tension, flash point, heat of combustion, boiling point distribution, cetane number, and lubricity of each oxygenate-ALS blend were measured. Table 8 shows the properties of the oxygenate-ALS blends considered for engine testing. Nine test fuels including the ALS base fuel and the 8 oxygenate-ALS blends were selected from the choices in Table 8.

**Table 8. Oxygenate-ALS Blends Screened for Engine Test**

Oxygenate – ALS Diesel Blend	Fuel Code	Oxygenate Vol.%	NACE Corrosion	Cetane Number	Density g./cm <sup>3</sup>	Viscosity at 40°C cSt	Surface Tension	Lubricity HFRR at 60°C µm
ALS – Base Reference Fuel	A	0	Passed	65.5	0.8169	2.94	30.3	483
Methylal (DMM)		16.06	NA	62.9	0.8217	1.67	28.4	503
Di-butyl maleate – ALS	I	21.64	Pass-B	57.7	0.8537	2.78	31.1	268
Tributyrin – ALS	H	18.35	Pass-B	52.6	0.8550	3.06	30.6	375
Di-ethyl adipate – ALS	G	18.76	Passed	56.0	0.8506	2.55	30.9	443
2-Ethoxy ethyl acetate – ALS	E	16.72	Pass-A	61.3	0.8397	2.10	31.0	490
2-Ethoxy ethyl ether – ALS	F	21.85	Passed	86.4	0.8342	2.09	31.0	670
Tri-propylene glycol mono-methyl ether – ALS	B	19.80	Pass-B	65.0	0.8416	2.73	30.5	505
Di-propylene glycol mono-methyl ether – ALS	D	19.42	Pass-B	61.4	0.8403	2.54	30.4	545
1-Methoxy-2-propanol – ALS	C	17.92	Passed	57.2	0.8321	2.19	30.8	495
<i>Other Candidates</i>								
2-Butoxy ethanol – ALS		24.05	Pass-B	59.6	0.8354	2.50	30.4	395
2,4,7,9-Tetra-oxa-decane (TOD) – ALS		13.82	Pass-A	64.5	0.8402	2.24	30.5	623

Of the oxygenate-ALS blends selected for engine testing in Table 8, the last three comprise a homologous series of mono-, di-, and tri-propylene glycol mono-methyl ethers. The propylene glycol mono-methyl ethers were included in the test matrix to determine the effect of oxygenate boiling point on PM emissions. Oxygenates selected for the engine test contained ether, ester and alcohol groups. The properties of the methylal-ALS blend are given in the table for reference. As noted above, 2,4,7,9-Tetra-oxa-decane was excluded because it was not available in amounts required for engine testing. 2-Butoxy ethanol was dropped from the list of viable candidates because of it was required in the amount of 25% by volume to make a blend containing 7 percent oxygen.

Figure 6 shows the TVF, dry PM and total PM emissions from the engine tests in chronological order. Except for Fuel Z, the fuel labels in Figure 5 are defined in Table 8. Fuel Z was an oxygenated diesel fuel produced by autoxidation of the ALS base fuel. Sparging pure oxygen through ALS diesel at about 160 °C produced Fuel Z. Fuel Z was prepared with an oxygen content of about 7 wt.%. It was included in the engine test phase of the study because it represented an alternative way of making oxygenated diesel fuel.

It is seen in Figure 6 that Fuel A was run first, once at each of 4 modes 5, 6, 10 and 11. Then Fuels B through Z were run consecutively in triplicate at mode 6. Fuel A was then run again once at each of the 4 modes. This was followed by triplicate runs on Fuels F through I and concluded with single runs on Fuel A at the operating modes 5, 6, 10 and 11. Fuel A was tested at modes 5, 10, and 11 because the original plan was to test the 2 most favorable oxygenate candidates at those modes. However, funds were not available to complete the engine tests on the oxygenated fuels at modes 5, 10 and 11.

The Mode 6 results in Figure 6 show that, except for Fuel Z, PM emissions from oxygenate fuels were substantially lower than the reference Fuel A (ALS). It is seen that the total PM emissions from the oxygenate-ALS blends, except Fuel Z, are similar, but distinctly different in the TVF and dry PM emissions. The TVF of PM from the oxygenated fuels was significantly greater than that of the reference Fuel A.

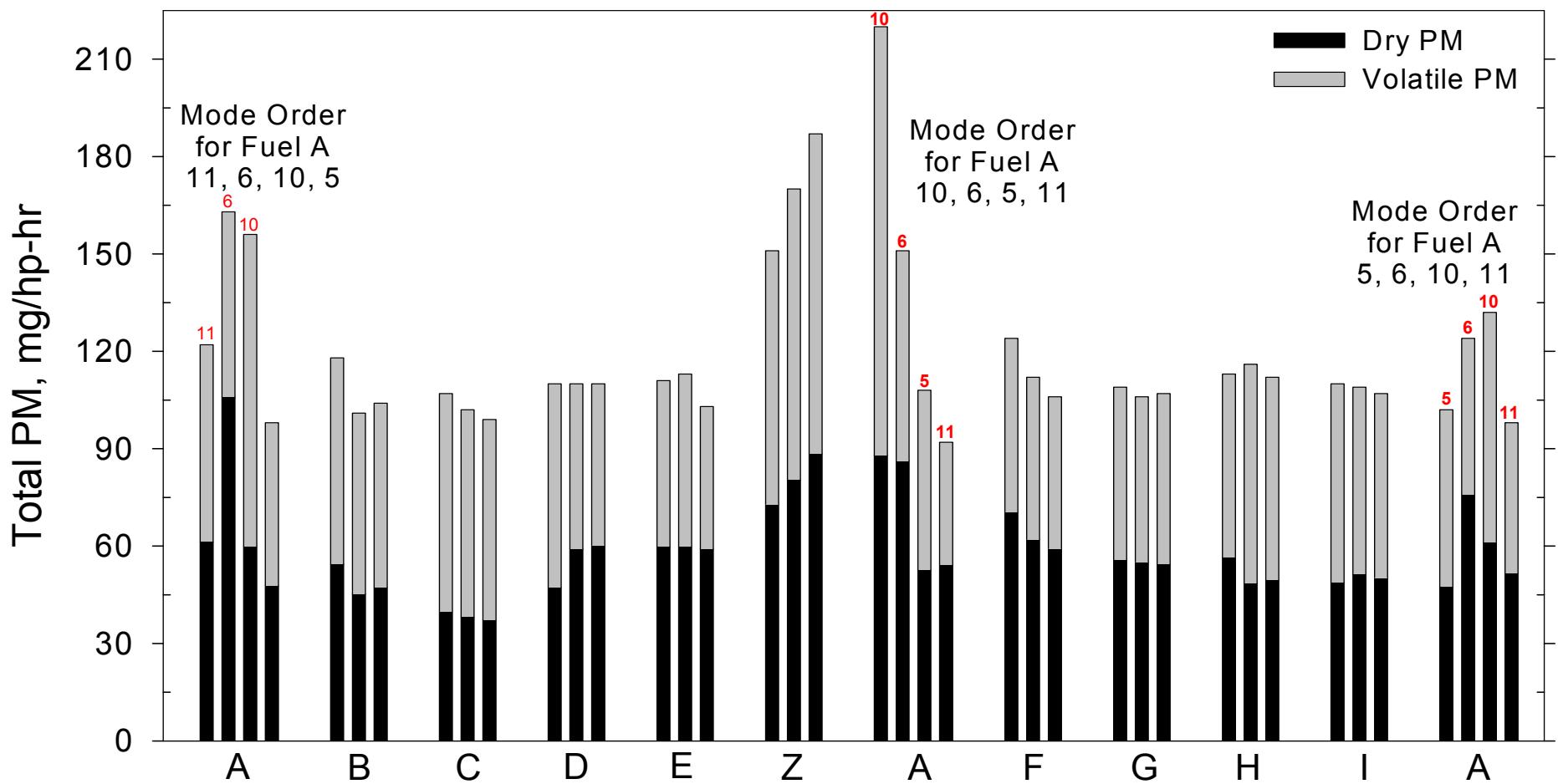


Figure 6. Total PM, dry plus volatile, emissions from test fuels run in a 2.2L Mercedes turbodiesel. Runs are in chronological order left to right. Reference fuel A was run at operating Modes 5, 6, 10, and 11. The oxygenated test fuels were only run at operating Mode 6.

Inspection of the results in Figure 6 suggests that the fuel run previously had an effect on the first run of the next test fuel. For example, the PM emission from the first run on Fuel B is higher than the second and third runs. The first run on Fuel D is questionable because the dry PM is lower and the TVF is higher than the second and third runs. The mode 10 run on Fuel A after Fuel Z was unusually high, and the first runs on Fuels F was significantly higher than the second and third runs.

The results in Figure 6 suggest that the fuel from a previously run either contaminated the next test fuel or affected the fuel injectors in such a way as to change the combustion process. The test procedure was designed to prevent fuel contamination. Before changing test fuels, the fuel lines and day tank were emptied and the pumps were run dry. Then the fuel system was flushed with one gallon of the new test fuel before starting the next test. The amount of fuel left in the engine fuel pump and injector lines was negligible, so the part of it that circulated back to the day tank would be so small that it would be doubtful that it would change the emissions.

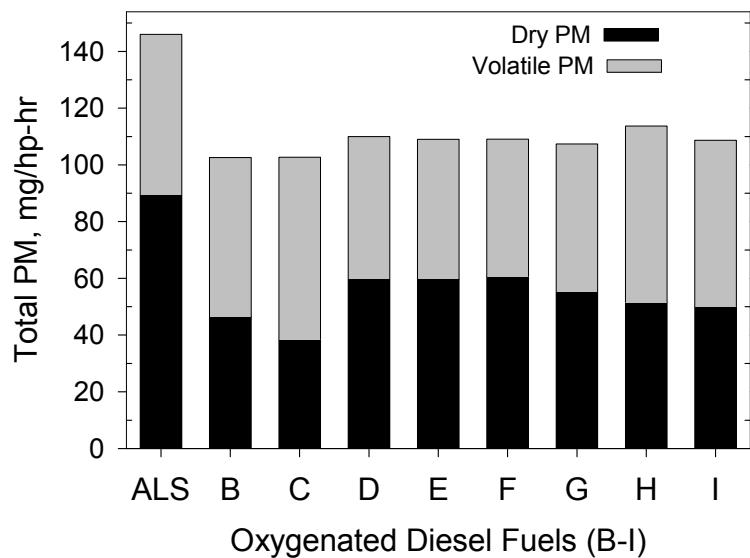
Even if a few ounces of fuel contaminated the day tank, it would be unlikely to have any affect after the engine was run for a while. No emissions data were taken until the engine was warmed up on the test fuel and all the engine parameters were stable. The engine was always run least 30 minutes on the new test fuel before emissions measurements were started.

An alternative to the fuel contamination explanation is that oxygenated fuels cleaned the fuel system and fuel injectors, which reduced soot formation. This is evidenced in Figure 5 by the fact that the PM emissions from Fuel A tended to decrease after the oxygenated diesel fuels were run. For modes 6 and 11 there was a monotonic decline in the PM emissions from Fuel A over the course of the engine testing. Fuel A emissions at mode 10 were dramatically higher after testing Fuel Z, but became lower after oxygenated Fuels F through I were tested. Fuel Z, which had a relatively high T90 and also contained a significant amount of soluble gum appeared to cause a temporary fouling of the injectors. The injector fouling appeared to be temporary because after running Fuel A

at mode 10, the PM emissions at modes 6 and 11 were lower than before the oxygenated diesel fuels were run. For mode 5, the PM emissions from Fuel A remained the same over the course of the engine testing and did not appear to be affected by oxygenated diesel fuels. Perhaps mode 5 was less sensitive to injector fouling because it was a higher power condition and required a higher injection pressure.

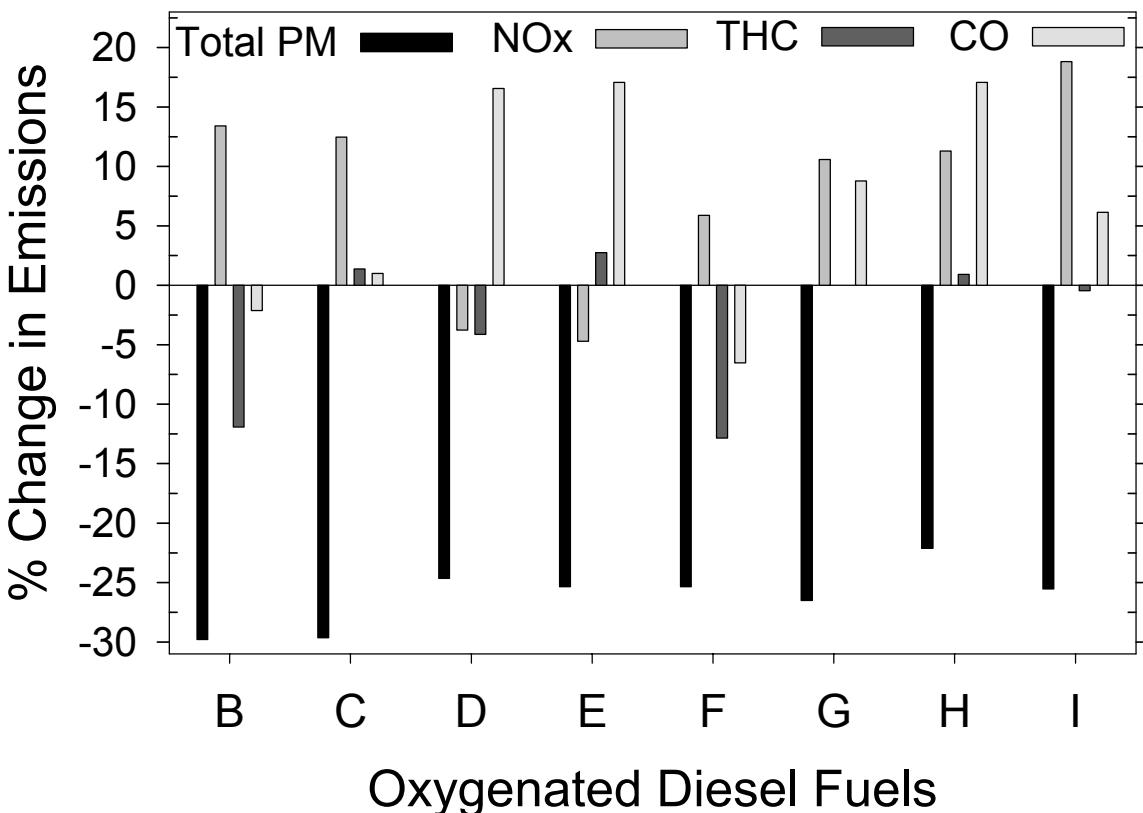
Based on the above analysis, the Ad Hoc committee decided that all 3 runs on Fuel Z and the first runs of Fuels B, D and F should be discarded. With these runs removed, Figure 6 shows the average total PM, TVF and dry PM emissions for the ALS base fuel and each of the oxygenate blends at operating Mode 6. While total PM emissions are statistically similar, the dry PM and TVF show significant variation among oxygenate diesel blended fuels. Also, oxygenated fuels have a higher TVF than the reference Fuel A. The increased TVF in PM from oxygenated fuels is important because it may well enhance the completeness of PM oxidation in catalytic after treatment devices.

Dry PM is believed to be a better indicator of sooting tendency than total PM because volatiles absorb on soot particles after the exhaust exits the combustion chamber. If it is assumed that the propensity to form soot correlates best with, dry PM, the results in Figure 7 suggest that oxygenate molecular structure plays a role in the soot formation mechanism.

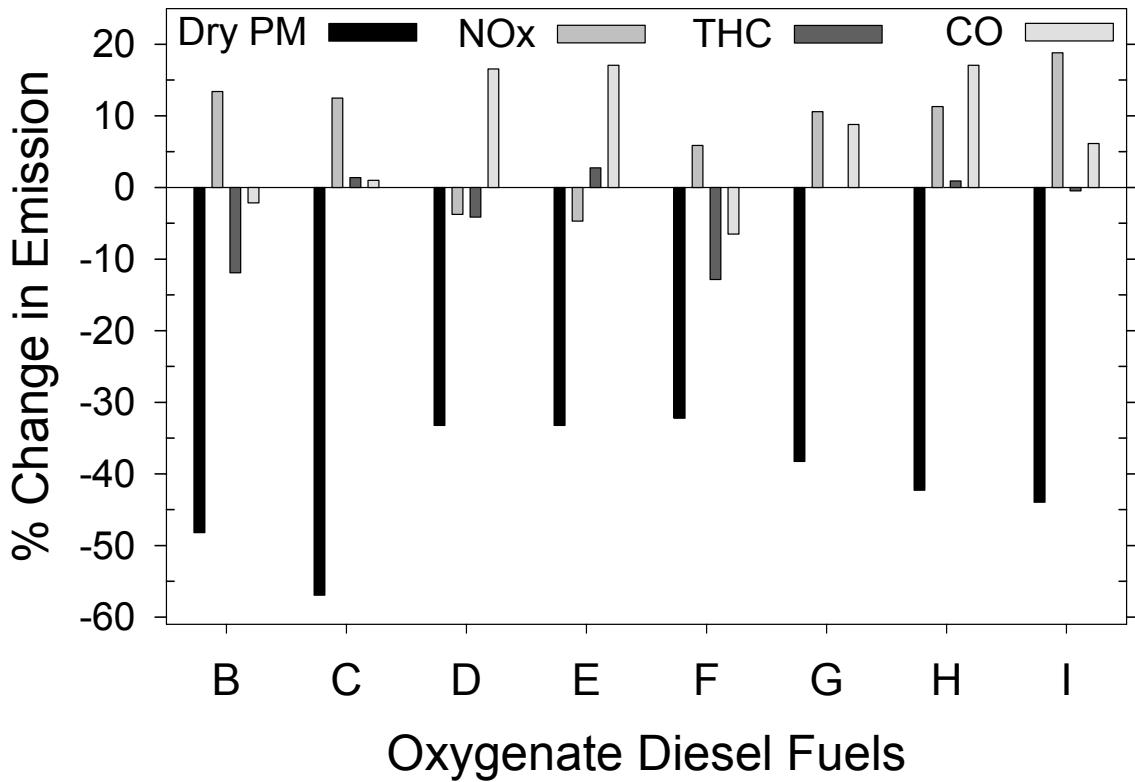


**Figure 7. Effect of Oxygenates on Average Amounts of Dry and Volatile Matter in the Total Particulate at Operating Mode 6 (2300 rpm, 4.2 bar).**

Before attempting to quantify the effects of oxygenates on dry PM emissions, it is important to consider the effects on the gaseous emissions. Figures 8 and 9 show the percent change in emissions from the oxygenated diesel fuels relative to the reference Fuel A. The gaseous emissions are compared with the total PM in Figure 8 and the dry PM in Figure 9. The figures show substantial differences in NOx and CO emissions among the test fuels. Oxygenates had little effect on total hydrocarbon (THC) emissions except for Fuels B and F. Fuels B and F are similar except for cetane number. Fuel F has a relatively high cetane number of 86, which indicates a shorter ignition delay, while Fuel B's cetane number (65) is similar to that of reference Fuel A. Since the start of injection, SOI, was always adjusted to achieve peak combustion pressure at 7 °ATDC, there should be no differences in completeness of combustion unless the flame speed is significantly affected by oxygenate type. Since oxygenate is unlikely to change the flame speed significantly, there appears to be no clear reason why Fuels B and F produced higher hydrocarbon emissions.



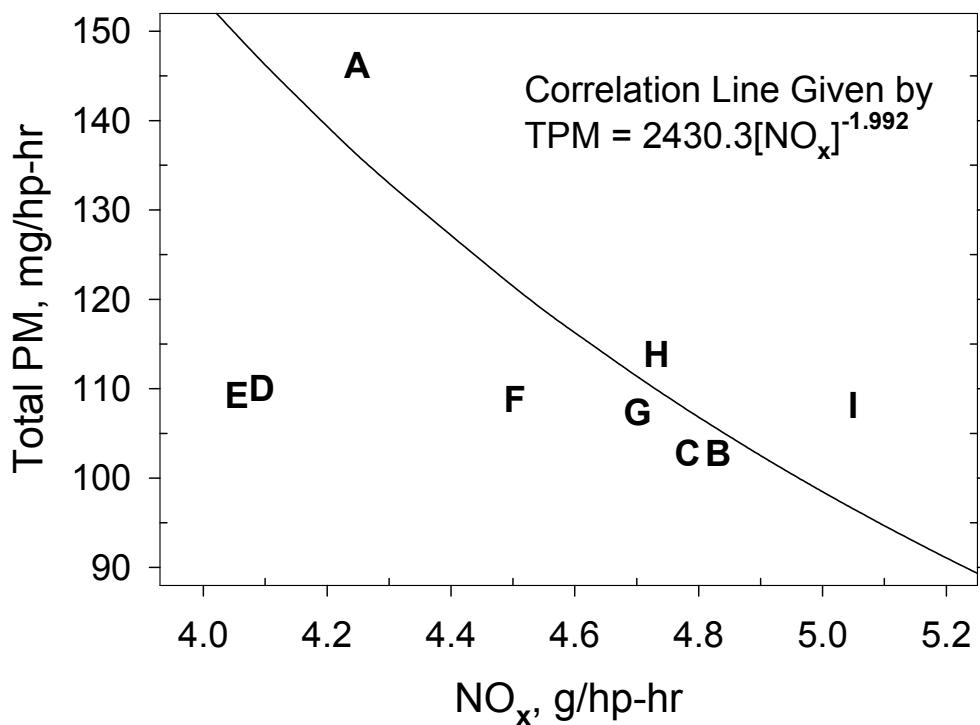
**Figure 8. The Chart Shows the Changes in Total PM and Gaseous Emissions from Oxygenated Fuels Relative to the Reference Fuel A.**



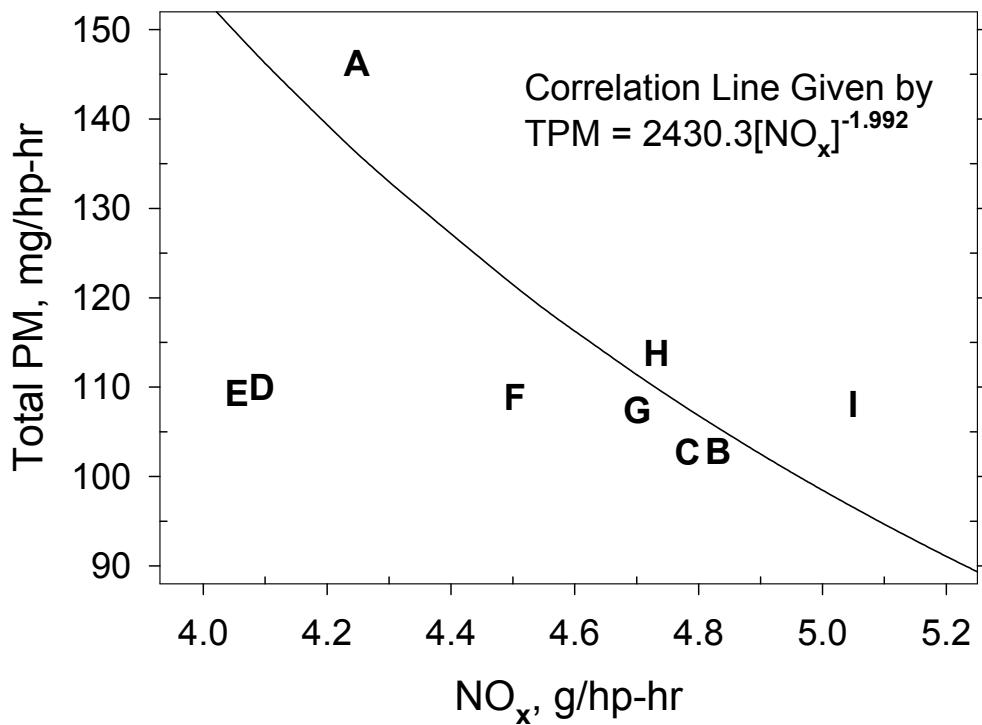
**Figure 9. The Chart Shows the Changes in Dry PM and Gaseous Emissions from Oxygenated Fuels Relative to the Reference Fuel A.**

Except for Fuels D and E the NOx emissions from the oxygenated fuels were higher than reference Fuel A. Fuels D and E also have relatively high CO emissions and they seem to be misplaced in the PM versus NOx plots shown in Figures 10and 11. Figure 10 shows total PM versus NOx and Figure 11 shows dry PM versus NOx. It is seen that all the fuels except D and E fall close to the curves in Figures 10 and 11.

The results on Fuels D and E were suspicious because these fuels were run on the same day. Inspection of the engine data revealed that when the engine was run on Fuels D and E, the BMEP was about 600 kPa instead of the usual 650 kPa recorded for the other test fuels. Inspection of the data showed the same power (torque and speed) and all the other engine parameters appeared similar. Even the thermal efficiencies of Fuels D and E calculated from their heats of combustion and brake specific fuel consumptions were similar to the other test fuels.



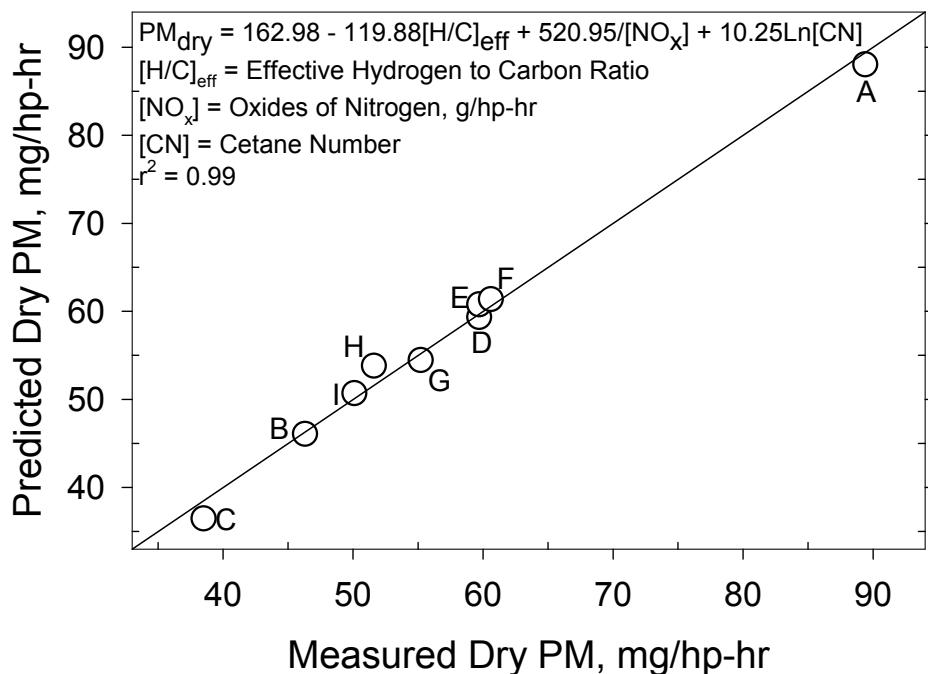
**Figure 10.** Relationship Between Total PM and  $NO_x$  Emissions from the Test Fuels. Data Points are Represented by Letter Names of the Test Fuels.



**Figure 11.** The Relationship Between Dry PM and  $NO_x$  Emissions from the Test Fuels. Data Points are Represented by Letter Names of the Test Fuels.

Because the NO<sub>x</sub> emissions from Fuels D and E were relatively low, even lower than the base reference Fuel A, it was suspected that the PM emissions from Fuels D and E would be high relative to the other test fuels, which had higher NO<sub>x</sub> emissions. Therefore, to compare the propensity to soot, it is necessary to take into account the relative NO<sub>x</sub> emissions of the test fuels. One approach to that is to correlate the PM emissions with the NO<sub>x</sub> emissions and the fuel properties that appear relevant to soot formation.

Figure 12 shows the results of correlating the dry PM emissions with the “effective hydrogen to carbon ratio,” the NO<sub>x</sub> emissions, and the cetane number. Table 9 gives the data used to create the correlation in Figure 12. Note that the dry PM emissions are used in the correlation because they are observed to be dependent on oxygenate type and they better represent soot formed in the combustion chamber. The T90 boiling point was not included in the correlation, because oxygenates had little or no effect on the T90 point of the blended fuels. The effective hydrogen to carbon ratio in Table 9 was calculated by multiplying the fuel-air ratio by the hydrogen to carbon ratio and dividing by the fuel-air ratio of Fuel A. Appendix 1 shows why the effective hydrogen to carbon ratio is equivalent to the product of the fuel-air ratio and the hydrogen to carbon ratio of the test fuel.



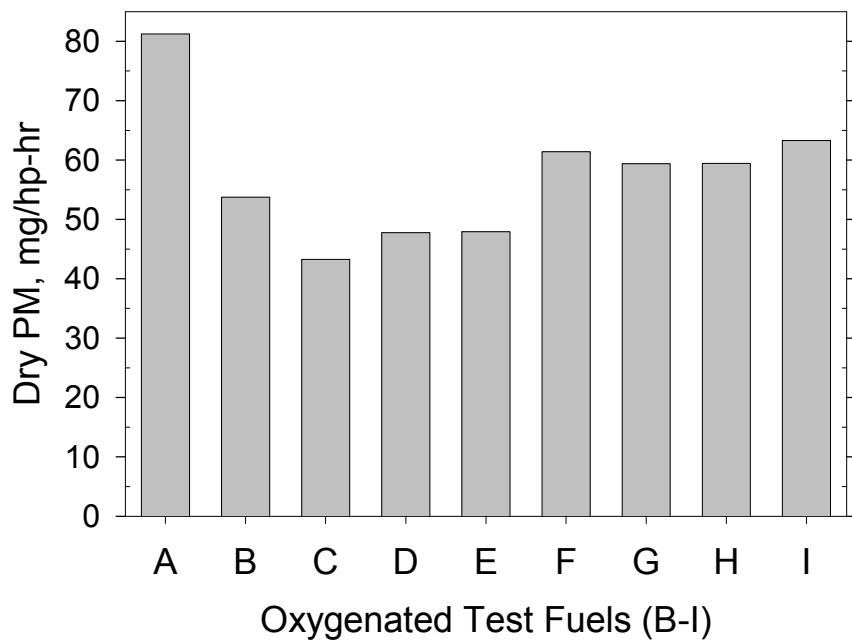
**Figure 12. Correlation of Dry PM Emissions with Effective H to C Ratio, NO<sub>x</sub> Emissions, and Cetane Number.**

**Table 9. Data used to create Figure 12.**

<b>Test Fuel</b>	<b>Dry PM mg/hp-hr</b>	<b>NOx g/hp-hr</b>	<b>Cetane Number</b>	<b>Fuel-Air Ratio</b>	<b>H – C Ratio</b>	<b>Effective H/C</b>
A	89.4	4.25	65.5	0.0267	2.005	2.005
B	46.3	4.82	65.0	0.0292	2.037	2.234
C	38.5	4.78	57.2	0.0298	2.070	2.310
D	59.7	4.09	61.4	0.0297	2.048	2.279
E	59.7	4.05	61.3	0.0303	2.004	2.277
F	60.6	4.50	86.4	0.0286	2.048	2.194
G	55.2	4.70	56.0	0.0294	1.971	2.174
H	51.6	4.73	52.6	0.0295	1.960	2.168
I	50.1	5.05	57.7	0.0295	1.938	2.144

Because it is observed that PM emission decrease as NOx emissions increase, a hyperbolic relationship was used to represent the effect of NOx on PM emissions. The cetane number is a relative measure of ignition delay time. Ignition delay time effects both NOx and PM emissions because it is the time allowed for evaporation and mixing of fuel vapors with air before ignition occurs. More complete mixing of fuel and air generally results in lower PM emissions and higher NOx emissions. The relationship between cetane number, CN, and ignition delay, I.D., is  $I.D. = k \ln(CN)$  where k is a proportionality constant. Therefore, according to the correlation equation in Figure 11, the dry PM emissions are directly proportional to the “effective hydrogen to carbon ratio” and ignition delay time, and inversely proportional to the NOx emissions.

Figure 13 shows the predicted dry PM emissions assuming that each fuel produced NOx emissions of 4.5 g/hp-hr. The bar chart indicates that Fuel B emits more soot than Fuel D, which in turn emits more than Fuel C. Fuels B is the tri-propylene glycol mono-methyl ether, Fuel D is the di-propylene glycol mono-methyl ether, and Fuel C is propylene glycol mono-methyl ether. These fuels were chosen for the engine test because they were of similar molecular structure, but had very different boiling points. Based on the predicted dry PMs of Fuels B, C, and D in Figure 13, it could be concluded that sooting tendency increases as oxygenate boiling point increases. However, oxygenates had very little effect on viscosity and essentially no effect on the T90 boiling points of the test fuels. The property that does appear to correlate is the “effective hydrogen to carbon ratio” given in Table 8. While it may be difficult to make a firm conclusion, the dry PM emissions data indicates that the sooting tendency correlates better with the chemical properties of the fuel than the physical properties.



**Figure 13. Dry PM Emissions Predicted Assuming All Fuel Produced the Same NOx Emissions of 4.5 g/hp-hr. Dry PM was Predicted Using the Correlation Equation in Figure 12.**

As discussed in Appendix 1, the “effective hydrogen to carbon ratio” is a function of the simple hydrogen to carbon ratio and the chemical bonding of oxygen to carbon in oxygenates. When oxygen is strongly bonded to carbon, the carbon is less free to be involved in the formation of soot so the effective hydrogen to carbon ratio of oxygenate is higher. In that respect, oxygenate molecular structure plays a role in soot formation since chemical bonding of oxygen with carbon causes differences in effective hydrogen to carbon ratio and sooting tendency.

## 5.1 Conclusions

The basic objective of this study was to select at least 2 oxygenates for future engine testing. But also included in the objective was to develop a better understanding of why oxygenates lower PM emissions. In the first approximation, PM emissions reductions were proportional to the oxygen content of the fuel. All of the oxygenated test fuels contained 7 wt.% oxygen and their total PM emissions were similar, averaging 26.1 percent below that of reference Fuel A. There was some spread in the total PM emissions (ca. 7%), but it was nothing like the spread in the dry PM (24%). The wide spread in the dry PM emissions indicated that fuel properties other than oxygen content play a role in the soot formation mechanism. Dry PM

emissions was found to correlate with the “effective hydrogen to carbon ratio” and the cetane number of the fuel. The effective hydrogen to carbon ratio is essentially the ratio of hydrogen to carbon that is not bonded to oxygen in the fuel.

While selecting oxygenates for future engine testing, the Ad Hoc committee concluded that the selection should be based on total PM emissions instead of dry PM emissions. In considering total PM emissions, Fuels B and C gave the greatest reduction (ca. 29.7 percent) and Fuel H gave the lowest reduction of about 22 percent. Fuels G and I appeared to be second to Fuels B and C. Fuel C, which had a low flash point, was tested to help understand the soot formation mechanism, so even though it showed promise in reducing PM emissions it could not be considered as an oxygenate candidate for future engine testing. Therefore, the most promising candidates for future engine testing were Fuels B, G and I. However, before selecting the final candidates, other factors such as economics of production, elastomer compatibility, toxicity and biodegradability had to be considered.

## 6.0 ELASTOMER COMPATABILITY

The elastomer compatibility of seals with fuel is especially important in the high-pressure injection pumps used in modern diesel engines. Incompatibility of fuel with elastomers may seriously degrade normal pump operation. Table 10 shows the matrix of 5 types of elastomers, 8 test fuels, and the 3 properties measured. The test specimens were O-rings, 2 Viton fluorocarbons (V-type) and 3 nitriles (N-type) elastomers commonly used in fuel system applications. The O-ring specimens were stressed in the test fuels for 500 hours at 40°C. Storage tests were conducted by suspending the O-rings in 50 mL of test fuel in sealed glass vessels.

**Table 10. Test Matrix of Elastomers, Test Fuels, and Types of Measurements**

Code – Elastomer Description	Test Fuels	Measurements
N674 – General Purpose Nitrile N0497 – High Aceto-Nitrile Content for Increased Fuel Resistance. N1059 – Peroxide Cured E.R. Nitrile V747 – Flourocarbon Carbon Black Filled V884 – Flourocarbon No Carbon Black	ALS Reference Fuel A TGME – Fuel B MGME – Fuel C EEA – Fuel E EEE – Fuel F DEA – Fuel G GTB – Fuel H DBM – Fuel I	O-Ring I.D. O-Ring Thickness Break Load and Tensile Strength

Each test fuel was placed in a vessel with 5 O-rings, one of each type shown in Table 10. The measurements shown in Table 10 were made immediately after the specimens were removed from storage so the absorbed fuel components would not be lost to evaporation.

The compatibility of fuel with elastomers was characterized by changes in dimensions, "Swell," and Tensile Strength. Swell is caused by the absorption of fuel components. O-ring Swell is measured in terms of increased O-ring diameter and thickness. Tensile strength was measured in terms of the break load force and the cross-sectional area of the O-ring. The Break Load is the force required to stretch the O-ring to the breaking point. The Tensile Strength is the pressure calculated from the Break Load force and the O-ring thickness. It is a measure of how much the O-ring can be stretched before it brakes.

## 6.1    **Swell**

The effect of the test fuels on Swell is shown in Figures 14-17. Figures 14 and 15 show the effect the on the O-ring diameter, and Figure 16 and 17 show the effect on O-ring thickness. Figures 14 and 16 show the absolute values of O-ring diameter and thickness respectively, while Figures 15 and 17 show percentage change in the parameters relative to the virgin elastomer not exposed to fuel. Reference Fuel A gave essentially the same result on diameter and thickness as the virgin elastomer, which was measured without any fuel contact. In general the oxygenated fuels caused an increase in O-ring diameter and thickness relative to reference Fuel A. Swell was particularly high in the Viton elastomers V747 and V884. The charts show N0497 (High Aceto-Nitrile Content) to be most resistant to swell in the oxygenated test fuels. The compatibility of fuels with the N0497 elastomer ranked in the order of A, F, H, B, E, C, G and I.

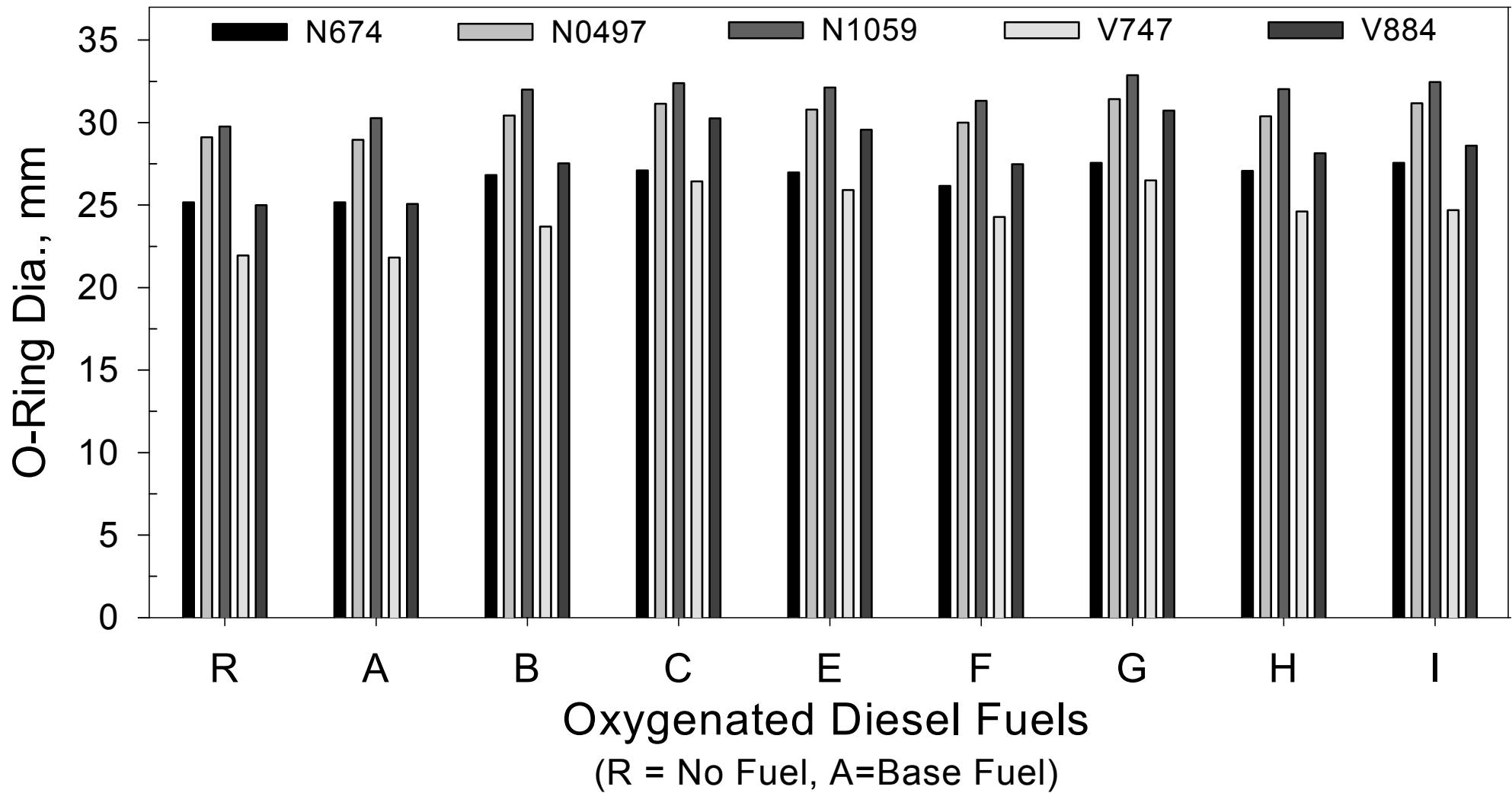


Figure 14. The Effect of Fuel on O-ring Diameter. Increased Diameter Indicates Swell Caused by Absorption of Fuel Components.

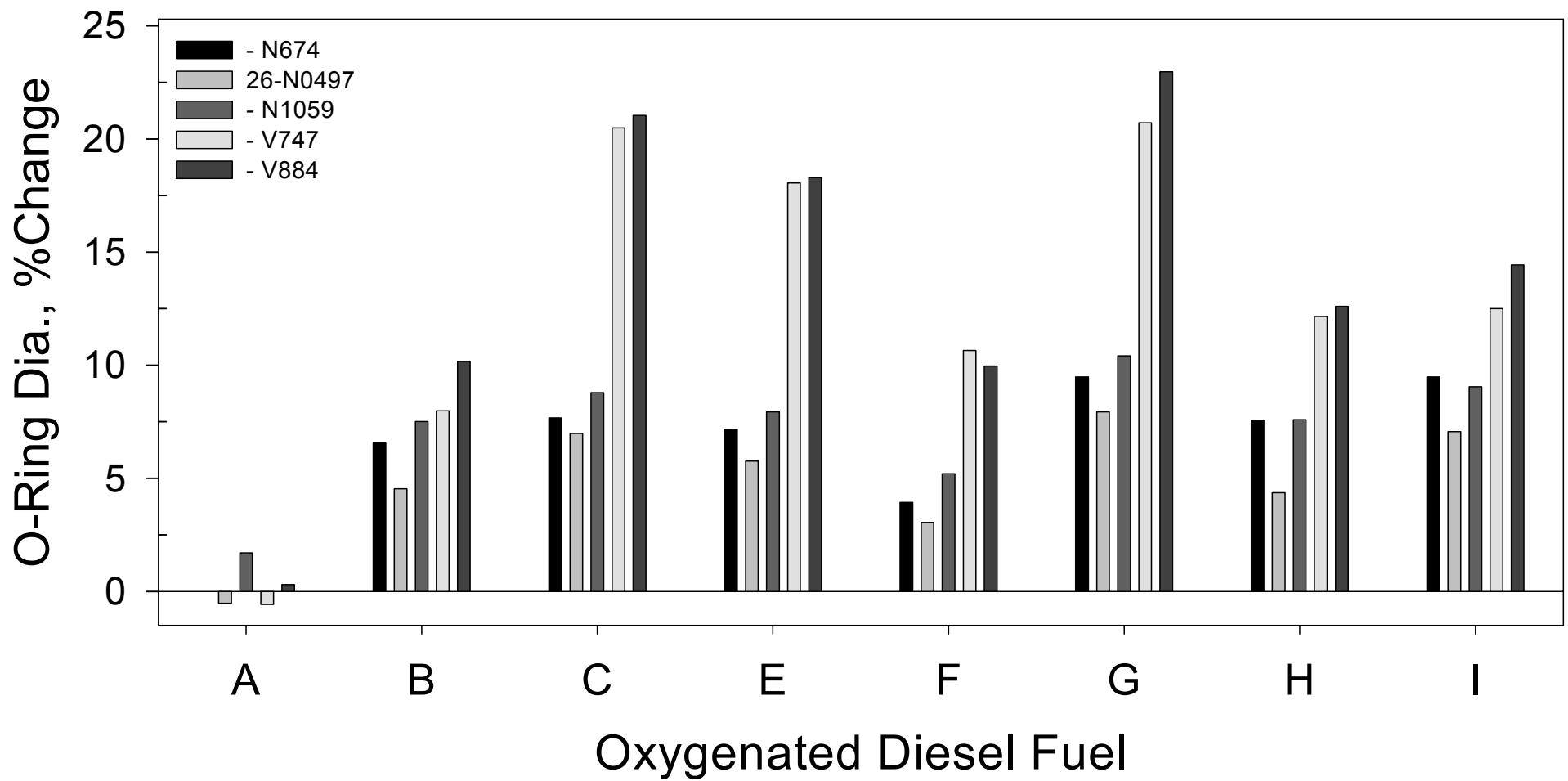


Figure 15. Effect of Fuel on O-ring Diameter. Percentage Change Calculated Relative to the Virgin O-ring (R) Unexposed to Fuel.

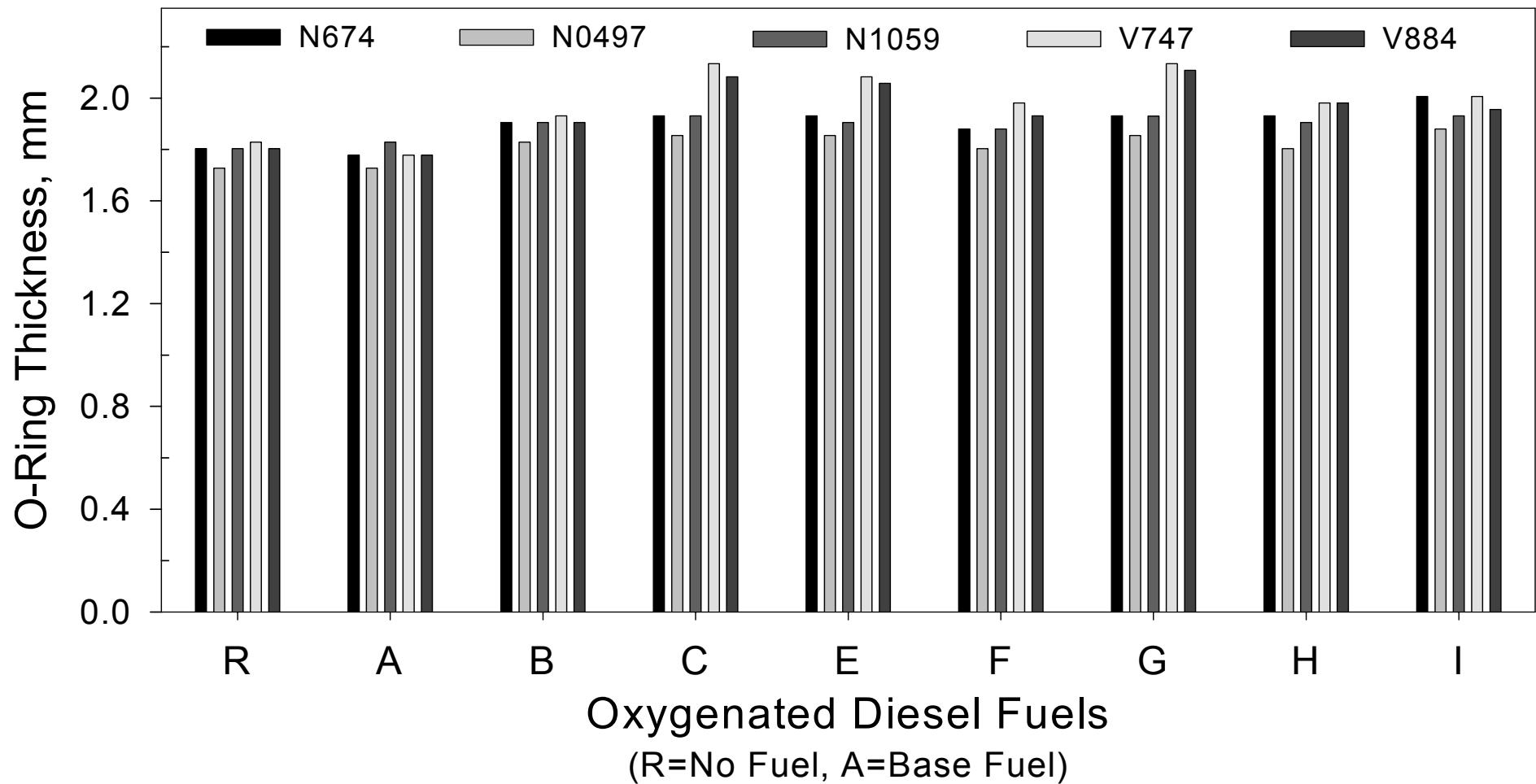
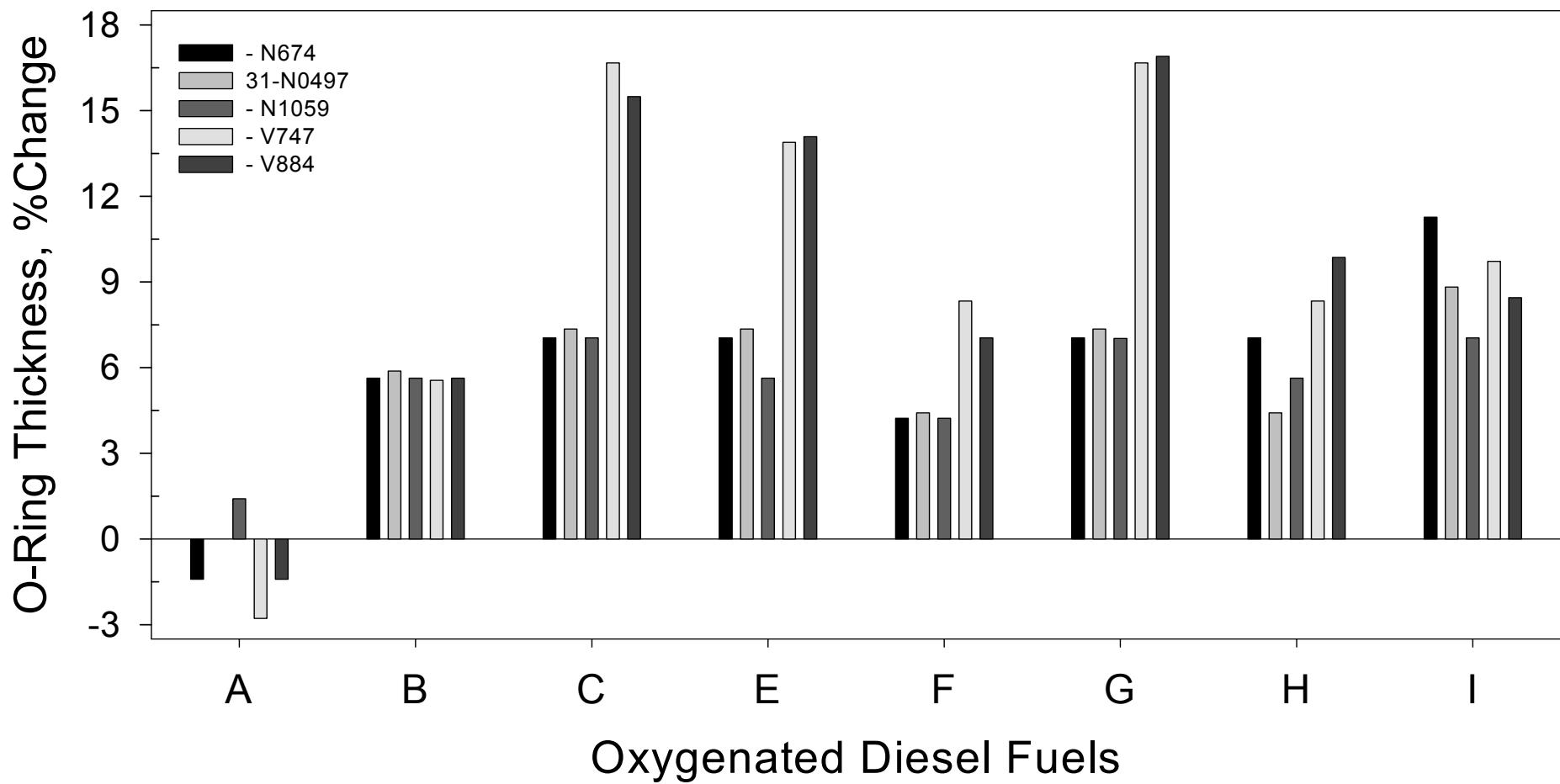


Figure 16. Effect of Fuel on O-ring Thickness. Increased O-ring Thickness Indicates Swell Caused by Absorption of Fuel Components.



**Figure 17. Effect of Fuel on O-ring Thickness. Percentage Change Calculated Relative to the Virgin O-ring (R) Unexposed to Fuel.**

## **6.2 Strength**

The effect of the test fuels on elastomer Tensile Strength is shown in Figures 18 and 19. Figure 18 shows the absolute values of the Tensile Strength and Figure 19 shows the percentage change in the Tensile Strength relative to the virgin elastomer not exposed to fuel. Except for N674 elastomers were either not affected or gain strength when exposed to reference Fuel A. All of the elastomers suffered significant loss in strength when exposed to the oxygenated test fuels. The loss in Strength was particularly evident in the V747 and V884 fluorocarbon based elastomers. As was the case with swell, the strength measurements also show N0497 to be most compatible with the oxygenated test fuels. The compatibility of fuels with the N0497 elastomer ranked in the order of A, H, I, G, B, F, E, and C.

## **6.3 Conclusions**

The oxygenated fuels caused considerable swelling and loss in tensile strength of the 5 elastomers tested. The fuel effects were much more ravaging on the Viton type elastomers than the Nitrile type. The high aceto-nitrile containing N0497 elastomer was most compatible with the oxygenated test fuels. Considering both swell and strength measurements on all the elastomers tested, the Ad Hoc committee ranked the test fuels in the order of A, B, F, H, I, C, E and G.

## **6.4 Other factors**

Other Factors important in selecting the appropriate oxygenates for diesel-fuel include cost of production, toxicity and biodegradability. Production economics is discussed and evaluated below. Evaluations of toxicity and biodegradability are also give, background information on Toxicity and Biodegradability are given in Appendices 2 and 3 respectively. All of the properties and test results are summarized in Table 13 and conclusions are drawn on oxygenate selection at the end of this report.

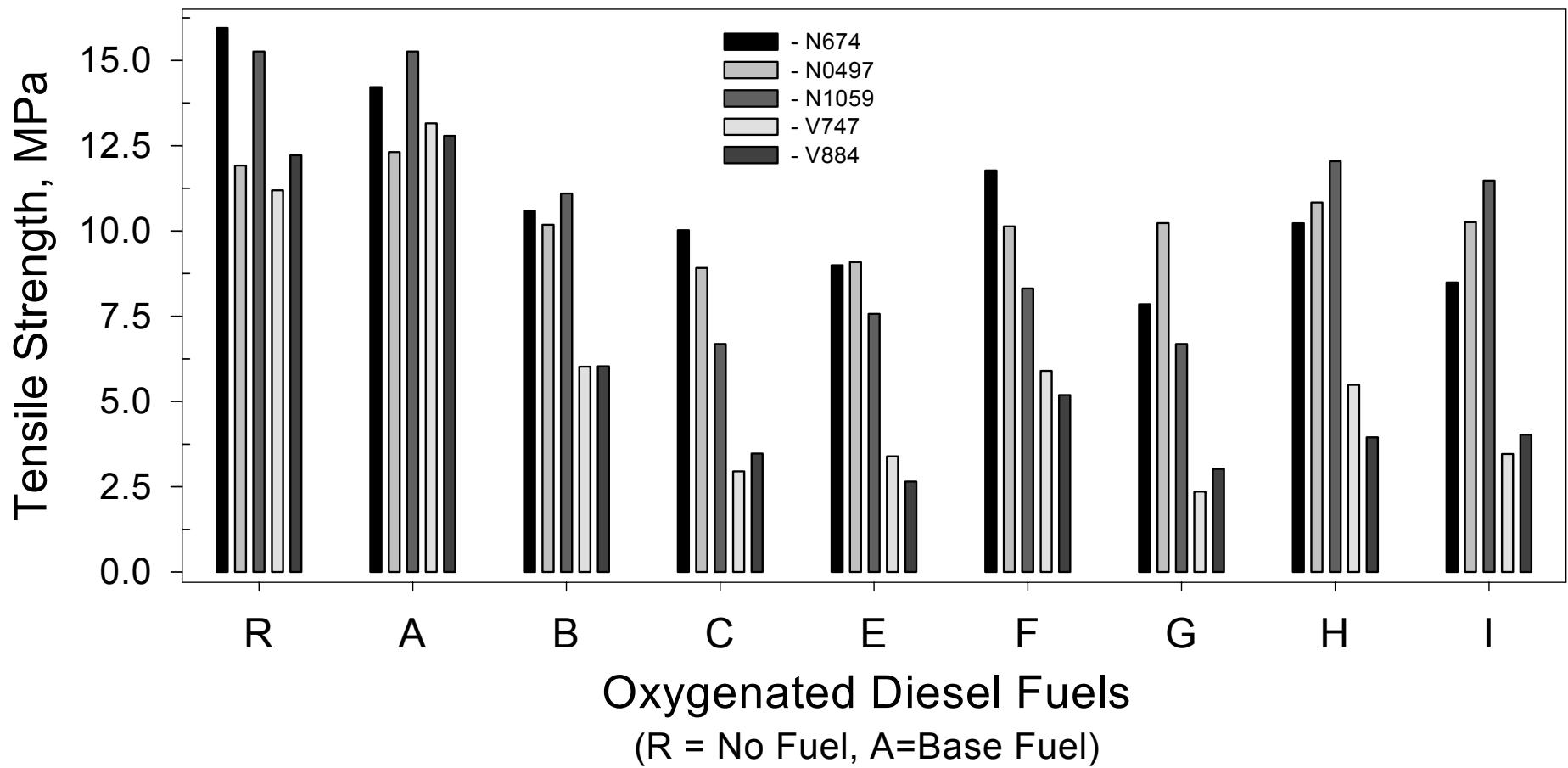


Figure 18. Effect of Fuel on O-ring Tensile Strength determined from O-ring Thickness and the Stretching Force Required to Break the O-ring.

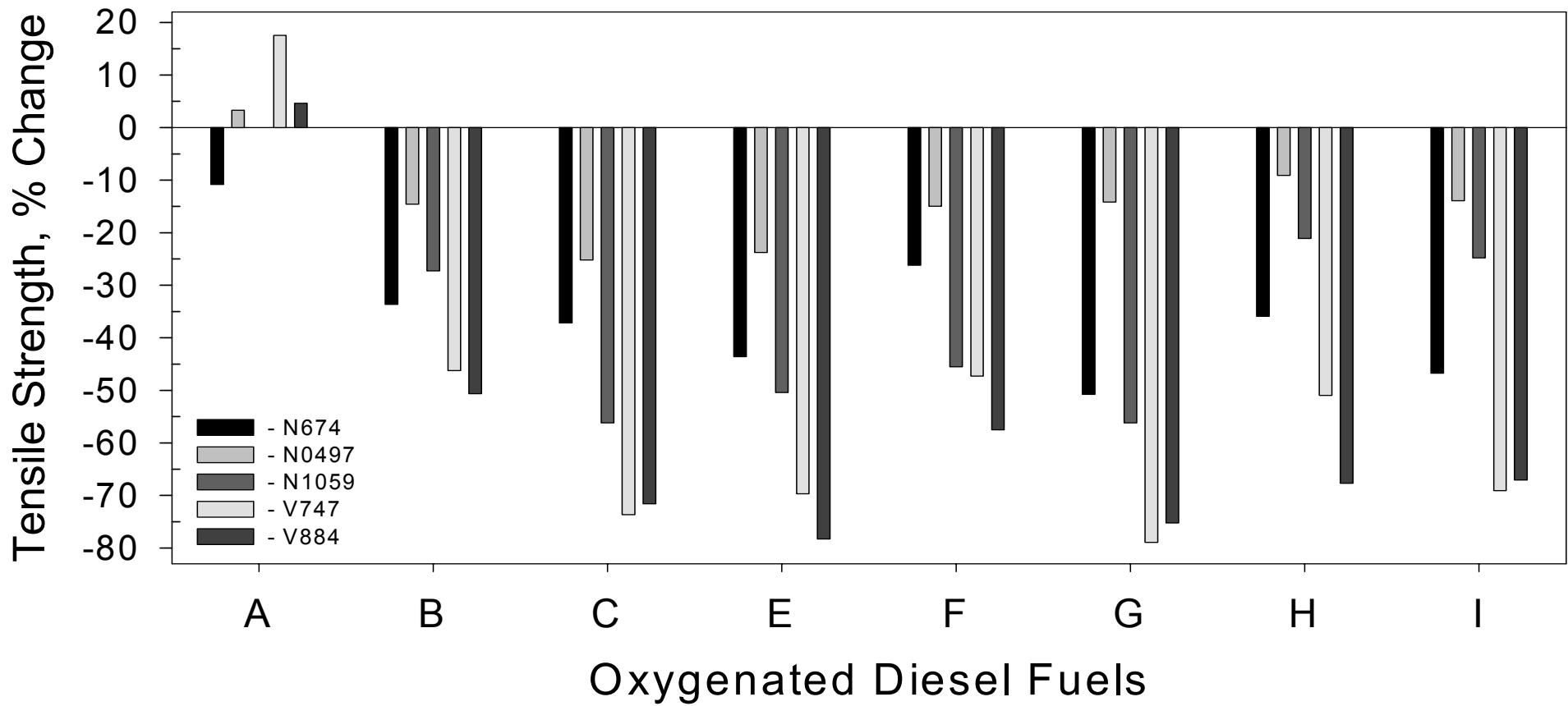


Figure 19. Effect of Fuel on O-ring Tensile Strength. Percentage Change Calculated Relative to Virgin O-ring (R) Unexposed to Fuel.

## **7.0 PRODUCTION ECONOMICS**

The objective was to obtain a relative estimate of oxygenate costs (using only basic raw materials) if the oxygenates were made on a scale appropriate for the fuel industry. The raw materials used were crude oil, natural gas, propane, butanes, ethylene, hydrogen, oxygen, and nitric acid. The last four deserve comment because they don't fit the term "basic raw materials" as it might be used in the fuel industry. Ethylene was used because it is made in such large quantities that a dedicated ethylene plant might not take full advantage of economies of scale. Similarly, hydrogen, oxygen, and nitric acid are all available in significant quantities. The method of providing any of these would be highly site specific, and site factors could not be a variable in a study of this sort. It seemed fair to simply charge a rate for them.

Source of raw material prices: Platt's Oil Price Handbook and Oilmanac for 1997. The crude oil price for West Texas Intermediate averaged \$20.61 for the year. Propane was \$0.374/gallon, n-butane was \$.429/gallon, and i-butane was \$.466/gallon.

All oxygenate plants were sized at 20,000 barrels per day of oxygenate. The major process units (plants) making intermediate products were sized to provide just enough feed for the oxygenate plant. Plant fixed investment costs were obtained from the SRI International PEP Yearbook for 1996, adjusted for size difference using Yearbook exponents and further adjusted for inflation using the Nelson-Farrar index. Yearbook values were also used for process yields, base number of operators per shift, and for utilities and chemicals requirements. In cases where the exact process was not available in the PEP Yearbook, similar processes were used.

The assumptions listed below in Table 11 were used to make the economic analysis.

<b>Table 11. Factors Used in Cost Estimates</b>	
Construction ("miraculous" or instantaneous)	First Year
Depreciation life	15 years
Salvage value	10 %
Depreciation method	Double declining balance
Income tax rate	37.4%
Return on investment	10%
Inflation (applied to product oxygenate price)	4%
Plant operating days	344 per year
Operators-per-shift plant-size adjustment exponent	0.23
Operator pay rate	\$20/hour
Labor load factor*	4.7
* Supervision, overhead, benefits, lab support, etc.	

Inflation was applied to the product price, but not to the raw materials.

The minimum plant-gate prices of the corresponding oxygenated diesel fuels were calculated using \$.548/gallon (Platt's 1997 price, low sulfur, U.S. Gulf Coast) as the minimum plant-gate diesel fuel price. The results are summarized in Table 12:

<b>Table 12. Estimated Costs of Oxygenates and Product Fuel with 7% Oxygen</b>				
<b>Fuel Code</b>	<b>Oxygenate</b>	<b>Blend %</b>	<b>Oxygenate \$/Gal</b>	<b>Fuel \$/Gal</b>
A	Base Fuel (ARCO Low Sulfur)	0	0.00	0.548
B	Tri-propylene glycol monomethyl ether	19.80	2.02	0.840
C	1-Methoxy-2-propanol	17.92	2.02	0.813
D	Di-propylene glycol monomethyl ether	19.42	2.02	0.835
E	2-Ethoxy ethyl acetate	16.72	2.05	0.800
F	2-Ethoxy ethyl ether	21.85	2.49	0.972
G	Di-ethyl adipate	18.76	4.58	1.304
H	Tributyrin	18.35	2.13	0.838
I	Di-butyl Maleate	21.64	2.03	0.870

## 7.1 Cost Estimates

The following paragraphs outline the basis for making the cost estimates. The estimates in Table 12 are preliminary and intended to invite comment on making improvements. Obviously, innovations in the synthesis and production will lower prices in the future.

### **7.1.1 Di-butyl Maleate**

The raw materials were natural gas, propane, and normal butane. The natural gas was reformed to make synthesis gas. The propane was dehydrogenated to make propylene for reaction with the synthesis gas to make butanols, 90% normal and 10% iso. The normal butane is oxidized to maleic anhydride to react with the mixed butanols to produce di-butyl maleate. The most capital-intensive operations are those for making propylene and maleic anhydride.

### **7.1.2 Propylene glycol methyl ethers**

The raw materials were natural gas, propane, isobutane, and oxygen. The natural gas is used to make methanol, and the propane is dehydrogenated to propylene, which is then oxidized to propylene oxide. The isobutane is oxidized to make tert-butyl hydroperoxide and tert-butyl alcohol byproduct. The peroxide is used with the propylene to make propylene oxide for insertion into the methanol. The molecular weight of the ether depends on the number of propylene oxide units inserted, and the three ethers, 1-methoxy-2-propanol, di-, and tri-propylene glycol monomethyl ether are coproduced. The propylene oxide plant is by far the most expensive operation and accounts for over half of the total capital requirement, but it also provides additional cash flow from the tert-butanol byproduct.

### **7.1.3 Tributyrin**

The raw materials were natural gas and propane. The propane is dehydrogenated to propylene, which is used for producing both glycerine and n-butyraldehyde. The natural gas is reformed to make synthesis gas used in a hydroformylation reaction with the propylene to make the n-butyraldehyde. This process also makes about 10% isobutyraldehyde, deemed acceptable in a fuel grade product, and the overall yield was increased to include it. The mixed butyraldehydes are oxidized with air and the product butyric acid is recovered by distillation. The analogous reaction for making acetic acid produces methyl acetate byproduct, a valuable ester. For making butyric acid, a mixture of esters were assumed with only half the value of methyl acetate for a byproduct credit. A portion of the propylene stream went to make glycerine via allyl chloride and

epichlorohydrin. In this step, the propylene cost only amounts to about one-third of the raw materials costs; chlorine and caustic soda are the other major contributors, and minor quantities of additional chemicals are used. Finally, the glycerine and butyric acid were esterified to make tributyrin.

#### **7.1.4 2-Ethoxy ethyl ether**

This ether is probably made by dehydrating two moles of 2-ethoxy ethanol. Ethylene is the principal raw material and is used to make both ethylene oxide and ethanol. Ethylene glycol ethyl ether (2-ethoxy ethanol) is made by inserting a single mole of ethylene oxide into ethanol. The dehydration to make the 2-ethoxy ethyl ether is probably made in sulfuric acid in a manner analogous to the production of ethyl ether. Economic information was lacking on that step, so it was tentatively modeled on an esterification process assuming a 90% of stoichiometric yield of 2-ethoxy ethyl ether from the 2-ethoxy ethanol. That operation accounted for about 15% of the capital. If the real etherification plant should turn out to be much more expensive, the cost estimate would need some upward adjustment.

#### **7.1.5 2-Ethoxy ethyl acetate**

The raw materials are ethylene and natural gas. The ethylene is used to make the 2-ethoxyethanol as described above. The natural gas is used to make methanol first, then acetic acid via carbonylation of the methanol. Economic data for making methanol were used for that step, then an incremental addition to the synthesis gas plant was made to provide the additional carbon monoxide for making the acetic acid. Economic data pertaining to this particular esterification was not readily available, so it was modeled by two other esterifications: ethyl and n-butyl acrylates.

#### **7.1.6 Di-ethyl adipate**

The raw materials are crude oil, ethylene, and nitric acid. The ethylene is used to make ethanol. Benzene is extracted from the hydrotreated and reformed naphtha, or reformate, and hydrogenated to make cyclohexane. Cyclohexane is oxidized to a mixture called KA oil, then further oxidized with nitric acid to make adipic acid. The adipic acid is

esterified with ethanol to make the di-ethyl adipate. Overall, the process is complex and has a high capital requirement, particularly for making the adipic acid. The use of nitric acid accounts for only about 10% of the raw material costs.

## **8.0 TOXICITY**

Toxicological data on oxygenates selected for engine testing were obtained from the literature. In several instances there were no data available on oxygenates of concern. Table 13 gives a summary of the data found on oxygenates tested in the 2.2 L Mercedes turbo-diesel.

The following are summary toxicological reports on oxygenates for which data could be found.

### **8.1 Tripropylene Glycol Monomethyl Ether (TGME) (CAS # 20324-33-8)**

Acute data from animal studies indicates that TGME has low acute toxicity. Union Carbide and ARCO Chemical have submitted to EPA acute and subchronic toxicity data (13- week inhalation study) that should be obtained (ARCO, Union Carbide). However, other sources confirm that the main effects of subchronic exposure seem to be narcosis and kidney toxicity (CHEMINFO, Patty's). No developmental toxicity was observed. In general, the propylene glycols do not appear to have the same toxic potential as their ethylene glycol counterparts. Metabolism studies indicate that the urinary metabolites of TGME are similar to those found with Dipropylene glycol monomethyl ether (Patty's). From an environmental perspective, the bioconcentration potential is low, biodegradation is high and the material is practically non-toxic to aquatic organisms on an acute basis (Dow). The carcinogenic potential of TGME is unknown at this time; however, the glycol ethers as a group are not known carcinogens. According to secondary sources (CHEMINFO, Dow, Patty's) this compound does not have developmental toxicity as do some other glycol ethers. (See Ref. 26 to 31)

**Table 13. Summary of Information from Toxicology Reports**  
**ACUTE Tox Tests**

Original Toxicity Rating	Proposed Overall Program Ranking	Fuel Code	Oxygenate - ALS Blend	Oral-Rat LD50 (mg/Kg)	Oral-Mouse LD50 (mg/Kg)	Oral-Dog LD50 (mg/Kg)	ACUTE Rating	Teratogen or Developmental Effects	Reproductive Effects	Mutagenicity Ames	Chronic Rating
LC*	9	A	ALSD Base Fuel for Reference	NA	ND	ND	U	U	U	U	U
LC	8	D	Di-propylene glycol mono-methyl ether	5400	ND	ND	Low	U	U	U	U
LC	7	C	1-Methoxy-2-propanol	NA	ND	ND	U	U	U	U	U
SC	6	E	2-Ethoxy ethyl acetate	low	ND	ND	Low	Significant	Significant	Negative	SC
SC	5	G	Diethyl adipate	1600	8100	ND	Low	Some	Potential	ND	SC
LC	4	F	2-Ethoxy ethyl ether	4970	ND	ND	Low	Not Significant	None Obsv	Negative	Low
SC	3	I	Di-butyl maleate	3730	ND	ND	Low	ND	ND	ND	U
LC	2	H	Tributyrin	3200	12800	ND	Low	Little Info	Little Info	Little Info	U
LC	1	B	Tri-propylene glycol monomethyl ether	3300	ND	5000	Low	Not Significant	ND	Negative	Low

\* LC=Lower risk based on limited data, SC=Some concern, ND=No data, U=Unknown

## **8.2 Tributyrin (CAS # 60-01-5)**

Tributyrin appears to have low acute oral toxicity, and has been approved, and routinely used, as a flavorant in butters and margarines (HSDB). It does not appear to be volatile, consequently inhalation exposures would not be of concern unless conditions generating aerosols or mists were in operation. There appears to be little known about the chronic effects of this material. Two older studies were conducted indicating tumorigenic potential, but the technical quality of these investigations has not been assessed. Recent studies indicate that a tributyrin diet induced an hypertrophy of the forestomach, an attribute that may have therapeutic value (Mosnier, et. al). (See Ref. 32 to 35)

## **8.3 Dibutyl Maleate (CAS # 105-76-0)**

Dibutyl maleate appears to have low acute dermal and oral toxicity, and low irritation potential based on animal studies and comparison to diethyl maleate (Patty's). However, two reports indicate that it is a strong sensitizer in humans, making it an undesirable compound in exposure situations where there is potential for direct contact. This was not confirmed or referenced elsewhere, including Patty's and a vendor MSDS (Acros Chemicals). Consequently, this health effect should be investigated. In general, maleates are readily hydrolyzed by the mammalian and bacterial systems and subsequently easily metabolized. Cumulative effects have not been observed (Patty's). (See References 36 to 41).

## **8.4 Diethyl Adipate (CAS # 141-28-6)**

It is thought that the polyacid esters are readily hydrolyzed by the GI tract, absorbed, readily metabolized and excreted (Patty's). In general, the adipic esters have low acute toxicities and slight irritation effects. Evaluation of seven adipates for embryonic-fetal toxicity and teratogenic effects in rats indicate that they are less toxic relative to the phthalates (Patty's), however there appears to be some fetal effects. While there was no increase in resorptions, mild increases in skeletal and gross malformations in the

offspring of diethyl adipate-treated rats (I.P. administration) were observed (REPROTOX). In addition, there appears to be a potential for reproductive effects (HSDB, REPROTOX), testicular toxicity (Nolte et al), and possible environmental effects that should be investigated (TOXLINE SEARCH). (See References 42 to 47)

## **9.0 BIODEGRADATION**

Biodegradation is the process by which a chemical is destroyed or transformed by living organisms—primarily bacteria and fungi. It can be the main removal mechanism of a contaminant in the environment, particularly in the subsurface. A chemical that resists biodegradation can accumulate or persist in soils, sediments, as well as surface and ground water. Typical examples of recalcitrant (i.e., resistant to biodegradation) chemicals that seriously affected the environment are DDT and branched alkyl detergents.

The introduction of MTBE as a gasoline additive to reduce air pollution and improve octane number unintentionally resulted in ground water contamination because of its limited biodegradation potential and relatively high water mobility. Concerns over water contamination have prompted the state of California to implement a phase out of MTBE in gasoline, which may extend to the rest of the nation in the future. Given this background, it is clear that the potential for biodegradation should be an integral part of the evaluation of candidate oxygenates for diesel fuel.

Experiments can be used to evaluate the potential of a compound to biodegrade, however, realistic biodegradation tests are too slow and laborious to be applied practically to a large number of candidate compounds. It is more efficient to start with a relatively quick elimination of unlikely candidates. For this purpose, a predictive approach can be used to separate compounds that are most likely to be recalcitrant from those that are most likely to be biodegradable. Predictions can be made based on structural similarities to compounds whose behavior is known. Relative times for biodegradability given in Tables 2 and 3 were estimated using models developed at Lawrence Livermore Laboratories.

## **10.0 SUMMARY**

Table 14 summarizes the results of all the tests performed and the properties of the oxygenates measured. According to the data in Table 2, the Ad Hoc committee has ranked the test fuels from 1 to 8 with 1 being the highest rating. The two oxygenates given the highest rating are tripropylene glycol monomethyl ether and di-butyl maleate. The evaluation was based on all the parameters, but certain properties, e.g., exhaust emission, toxicity, lubricity and cetane number played a somewhat more important role in the selection process. For example, tributyrin was originally in second place because it was relatively non-toxic and had better than average lubricity. It was reduced to third place because it caused a relatively large decrease (ca. 12 units) in the cetane number of the oxygenate – diesel fuel blend. Some decrease in cetane number can be tolerated, but a decrease of 12 numbers could result in a fuel blend with a cetane number less than 40.

**Table 14. Fuel Property Analysis and Engine Emissions Measurements**

Proposed Ranking & Label	Oxygenate – ALS Blend	Relative Emissions				Added Cost c/gal	Predicted Biodegradability Relative to Benzene	Elastomer Compatibility Ranking	Oxyg. Vol.%	Flash Point °C
		Total PM	Dry PM	NOx	Toxicity					
9-A	ALSD Base Fuel for Reference	100	100	100	LR*	0	NA*	1	0	88
8-D	Di-propylene glycol mono-methyl ether	75	62	96	LR	30	NR*	NR	19	77
7-C	1-Methoxy-2-propanol	70	43	112	LR	27	NR	6	18	35
6-E	2-Ethoxy ethyl acetate	75	67	95	SC*	26	1.25	7	17	62
5-G	Diethyl adipate	74	62	111	SC	76	1.35	8	19	91
4-F	2-Ethoxy ethyl ether	75	68	106	LR	43	0.73	3	22	78
3-H	Tributyrin	78	56	111	LR	29	1.36	4	18	91
2-I	Di-butyl maleate	74	56	119	SC	33	1.33	5	22	93
1-B	Tri-propylene glycol mono-methyl ether	70	52	113	LR	30	0.21	2	20	90

\* LC=Lower risk based on limited data, SC=Some concern, ND=No data, NA=No analysis, U=Unknown, NR=No result

**Table 14. Fuel Property Analysis and Engine Emissions Measurements (Continued).**

Proposed Ranking & Label	Oxygenate - ALS Blend	Lubricity, µm HFRR, 60°	Cetane Number	Viscosity CSt at 40°C	T90 °C	Density g/cc	Surface Tension Dynes/cm
9-A	ALSD Base Fuel for Reference	483	65.5	2.94	346	0.8169	30.3
8-D	Di-propylene glycol mono-methyl ether	545	61.4	2.54	342	0.8403	30.4
7-C	1-Methoxy-2-propanol	495	57.2	2.19	343	0.8321	30.8
6-E	2-Ethoxy ethyl acetate	490	61.3	2.10	344	0.8397	31.0
5-G	Diethyl adipate	443	56.0	2.55	340	0.8506	30.9
4-F	2-Ethoxy ethyl ether	670	86.4	2.09	342	0.8342	31.0
3-H	Tributyrin	375	52.6	3.06	342	0.8550	30.6
2-I	Di-butyl maleate	268	57.7	2.78	340	0.8537	31.1
1-B	Tri-propylene glycol mono-methyl ether	505	65.0	2.73	342	0.8416	30.5

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## **APPENDIX A**

**The Effective Hydrogen to Carbon Ratio in terms of the Fuel-Air Ratio and  
Hydrogen to Carbon Ratio of the Fuel.**

Figures 4 and 11 above show that the PM emissions from oxygenated fuels correlate with an effective H to C ratio. The effective H to C ratio accounts for carbon that is tied up with oxygen and is thus unlikely to be involved in the formation of soot. It assumes that carbon atoms tied up with oxygen atoms in the fuel can not participate in soot formation. The effective H to C ratio of a fuel containing oxygen may be expressed as

$$[\text{H/C}]_{\text{Eff}} = \text{H}/[\text{C-O}] \quad (1)$$

where H, C, and O are the relative numbers of hydrogen, carbon and oxygen atoms in the fuel respectively. Equation 1 implies that the mechanism of soot formation in oxygenated fuels is the same as that in pure hydrocarbons. The only difference between oxygenated fuels and pure hydrocarbon fuels is that the carbon bonded to oxygen does not participate in the formation of soot.

The correlation shown in Figure 11 assumes that

$$[\text{H/C}]_{\text{Eff}} = k[\text{F/A}] \times [\text{H/C}] \quad (2)$$

where  $[\text{H/C}]_{\text{Eff}}$  is the effective H to C ratio, F/A is the fuel-air ratio and H/C is the hydrogen to carbon ratio of the fuel. This relationship assumes that the fuels are all tested at the same engine power, i.e., the same torque and speed. It also assumes that the injection timing is adjusted to achieve the same location of peak combustion pressure for all test fuels. With engine power and location of peak pressure constant, the fuel-air ratio depends on the heat of combustion and the stoichiometry.

The objective is to show that  $[\text{F/A}] \times [\text{H/C}]$  is proportional to  $[\text{H/C}]_{\text{Eff}}$  assuming that the above mentioned conditions are true. The database for this analysis consisted of heats of combustion for 80 pure oxygenates [1]. Since gross heats of combustion were reported in the literature, they were converted to net heats of combustion. Based on empirical formulas and the net heats of combustion, the energy density, kcal/mole of combustible

mixture was calculated for all oxygenates at the same equivalence ratio. Since the work done in the combustion chamber depends on how much the combustion product gases expand, it was necessary to account for the change in moles in going from the reactants to products. The mole change was included in calculating the energy density of the combustible mixture. Note that the energy density of oxygenates varied by as much as 18 percent.

The fuel-air ratios were calculated to achieve the average energy density in the combustion chamber for all 80 oxygenates. In other words, the fuel-air ratios were adjusted to give an energy density that would be equal to the average of all 80 oxygenates. The correlating parameter “[F/A][H/C]” was obtained by multiplying the adjusted fuel-ratios with the H to C ratios of the oxygenates.

The effective H to C ratio was calculated as:

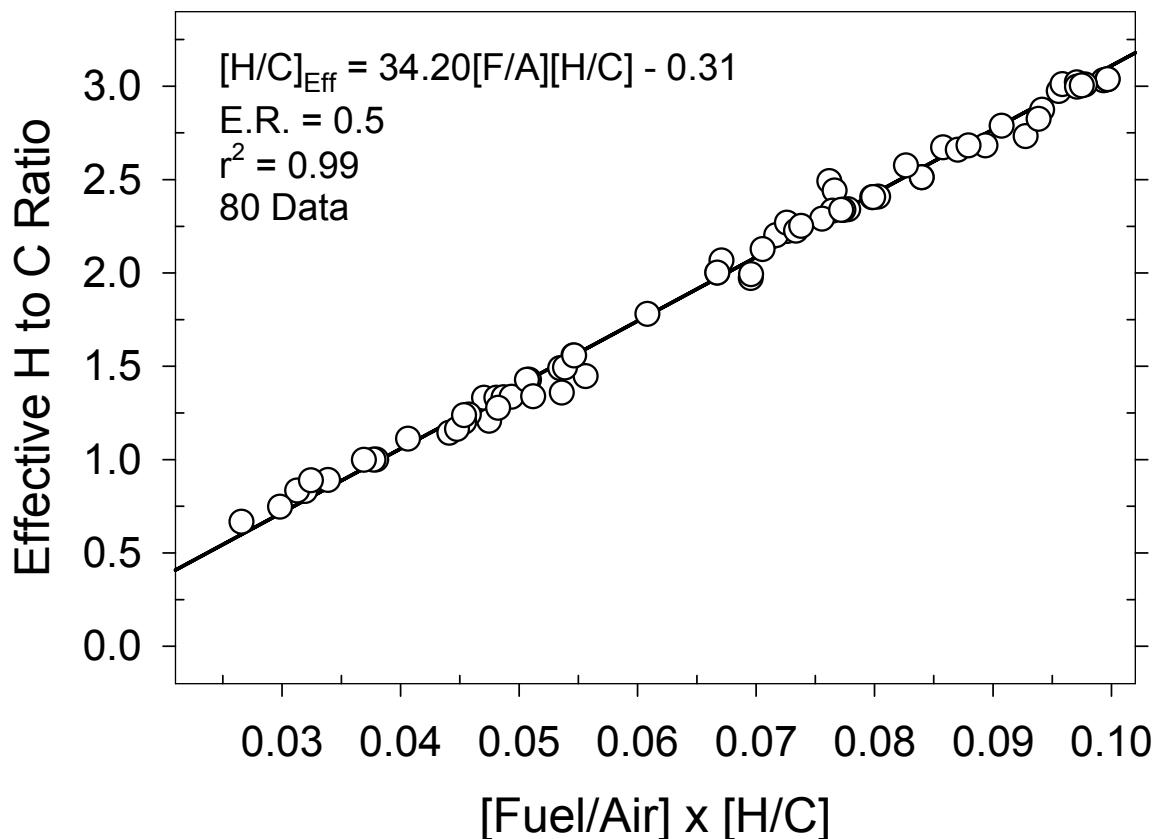
$$[\text{H/C}]_{\text{Eff}} = \text{H}/[\text{C}-k\text{O}] \quad (3)$$

where H, C, and O are the respective numbers of hydrogen, carbon and oxygen atoms in the oxygenate and k is a function of the energy density in the combustible chamber, ED, expressed as:

$$k = 1 + (\text{ED}_{\text{avg}} - \text{ED})/\text{ED}_{\text{avg}} \quad (4)$$

where  $\text{ED}_{\text{avg}}$  is the average energy density of the 80 oxygenates. Conceptually, k is a bias on the effectiveness of oxygen atoms to tie up carbon atoms and prevent them from participating in the soot formation process. For oxygenates that have less than average heats of combustion, the C-O bonds in the oxygenate tend to be stronger than average. The parameter k in Eqn. 4 is used to express the difference in the C-O bond strength in oxygenates.

Figure A-1 shows the correlation between the effective H to C ratio,  $[H/C]_{\text{Eff}}$  and the parameter,  $[F/A] \times [H/C]$ , used in Figure 11 to correlate dry PM with oxygenated fuel properties. It is seen that  $[H/C]_{\text{Eff}}$  is directly proportional to  $[F/A] \times [H/C]$ , indicating that the parameter  $[F/A] \times [H/C]$  is another way to express  $[H/C]_{\text{Eff}}$ .



**Figure A-1. Correlation of the Effective H to C Ratio,  $[H/C]_{\text{Eff}}$  with the Correlating Parameter,  $[F/A][H/C]$ , used to Correlate Oxygenate Fuel Properties with Dry PM Emissions from the 2.2 L Mercedes Turbodiesel (See Figure 11).**

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**APPENDIX B**  
**POTENTIAL TOXICITY OF OXYGENATES**  
**Biochemical Mechanisms: Metabolism, Adaptations, and Toxicity**

## **Introduction**

In the realm of “traditional” (i.e., human health oriented) toxicology, the study of biochemical phenomena occupies a central position. Elucidation of the biotransformation or metabolism of chemical compounds into more or less toxic products, of the underlying modes of toxic action, and of early biochemical responses have been accepted as critical to the informed diagnosis of human exposure to chemicals, as well as to the development of clinical treatments to counteract toxic effects. In aquatic toxicology, however, biochemical studies have played a lesser role. There are probably two reasons for this:

- Traditional toxicology is concerned ultimately with only one species – the human; other species are studied as models (rats, mice) for humans. The number of species of concern in aquatic toxicology, in contrast, is vast.
- In traditional toxicology, the biological level of chief concern in the individual organisms, is a person. In aquatic toxicology concern is principally for higher levels of organization – populations, communities and ecosystems.

In recent years, biochemical studies have received greater prominence in aquatic toxicology. This has occurred for several reasons:

- There is a growing appreciation that basic research into fundamental processes can provide a more solid theoretical foundation that can be applied to the problem solving endeavors of aquatic toxicology.
- There is cross-fertilization between aquatic toxicology and medical toxicology resulting from a growing realization that the issues of ecosystem health and human health are highly related and that continued isolation between scientists in these areas is inefficient and counter productive.

- Interest has increased in the development of sensitive biochemical based tools (“biomarkers”) for monitoring environmental quality. A key motion underlying biomarkers is that selected biochemical responses measured in feral organisms, for example, can provide sensitive indices, or early warning signals, for potential ecosystems degradation caused by contaminants. The development of biomarkers clearly illustrates a case in which basic research can yield practical tools that are the environmental equivalent of clinical diagnostics. In general, as an early warning of biological impact and as a predictable relationship between the physiological state of the organism and population-level parameters, biomarkers can play a significant role in ecological risk assessments.

Related to biochemical aspects of particular interest in aquatic ecosystems are the following:

- Enzyme systems that metabolize or biotransform, a broad array of organic contaminants.
- Protective and toxic responses associated with oxyradicals, the production of which is enhanced by many chemicals.

### **Biotransformation of contaminants**

Perhaps the most extensive studies of biochemical systems in aquatic animals related to toxicity of chemicals are the enzymes involved in the metabolism of transformation of organic chemical contaminants. Studies of the biochemistry and function of biotransformation enzymes are central in our understanding of the toxic effects of many foreign compounds. The activities of biotransformation enzymes influence clearance rates and therefore the degree to which xenobiotics bioaccumulate in an organism. Bioaccumulation potential in turn affects the level of exposure required to elicit toxic

effects. In addition, by changing the structure of that xenobiotic the toxicity of that compound can be drastically affected.

For bioaccumulation of a foreign compound to occur, the rate of uptake of that compound must exceed the rate of clearance. Many lipid-soluble compounds would accumulate almost indefinitely if the organism did not have a means of transforming them into water-soluble metabolites capable of being excreted. Biotransformation affects the toxicity of a foreign molecule by influencing not only the degree to which the molecule accumulates but also its reactivity with cellular macromolecules such as nucleic acids and proteins. Biotransformation is generally regarded as a protective mechanism to reduce the accumulation and toxicity of xenobiotics. However, there are numerous examples in which the product of detoxification enzymes is more toxic than the parent compound. A well-studied example of enzymatic “activation” is biotransformation of the common environmental carcinogen benzo[a]pyrene. This compound is not a carcinogen itself but requires enzymatic activation. There are also examples of synthetic compounds that must be enzymatically activated in order to exert their toxic effects. Organophosphate insecticides are examples of compounds that are activated by specific enzymatic systems.

Because of the inducibility of the biotransformation enzymes, there has been considerable effort to determine the feasibility of using these enzymes in environmental monitoring as biomarkers of contaminant exposure and effects.

## **Activated oxygen metabolism and oxidative stress**

### **- Oxyradicals**

Molecular oxygen ( $O_2$ ) is generally thought of as a benign compound; it is essential for aerobic organisms, which include all higher life forms. Its dominant role in eukaryotes is that of terminal electron acceptor in mitochondrial respiration, where it is ultimately reduced to water during the complex process of oxidative phosphorylation, the major source of ATP in aerobes. It is important to note, however, that the reduction of  $O_2$  to water requires four electrons, and this reduction proceeds sequentially through the one-,

two-, and three- electron products. These reduction products are superoxide radical ( $O_2^-$ ), hydrogen peroxide ( $H_2O_2$ ), and the hydroxyl radical ( $.OH$ ). These activated species, particularly  $.OH$ , are very reactive and potentially deleterious to biological systems. Both,  $O_2^-$  and  $.OH$  are oxygen-based free radicals (*oxyradicals*). Although not a free radical,  $H_2O_2$  is also reactive and it serves as an important precursor to  $.OH$ . Therefore, it is often treated as an oxyradical.

### **- Sources of oxyradicals**

In addition to mitochondrial electron transport, several other sources of endogenous cellular oxyradical production have been identified. However, in toxicological studies, oxyradicals are examined chiefly in relation to chemicals that enhance their production and the resulting damaging effects. Classes of compounds particularly noted for their ability to enhance the flux of oxyradicals include quinones and diols, bipyridils, aromatic nitro compounds, aromatic hydroxylamines, aromatic azo dyes, and transition metal chelates. A key mechanism by which many of these compounds enhance cellular production of oxyradicals is referred to as redox cycling. In this cycle, the compound is first reduced to its corresponding free radicals, with reducing equivalents typically provided by NADH or NADPH. These reactions are generally catalyzed by an enzymatic system. Both events can underlie the toxicity of redox-active compounds and toxic consequences. In general, the redox cycling analysis will include information about free radical production, antioxidant defenses and toxicological consequences.

### **- Oxidative damage**

Free radicals, including oxyradicals, can react with a large variety of biomolecules and are often nonspecific with respect to biochemical targets. This is particularly true regarding highly reactive radicals such as  $.OH$ . Fundamental lesions associated with oxyradicals include oxidation of membrane lipids, proteins, and nucleic acids and altered cellular redox status. These perturbations are believed to underlie specific tissue injuries associated with redox-active contaminants and, more broadly, may be associated with aspects of chemical carcinogenesis and aging. However, the understanding of the progression of events from a primary biochemical effects (e.g., oxidative DNA damage)

to an ultimate toxic expression (e.g., cancer) is in most cases incomplete. Between the examples of primary biochemical events associated with fluxes of oxyradicals are:

- Lipid peroxidation, the oxidation of polyunsaturated fatty acids (PUFAs) is an important consequence of oxidative stress and has been investigated extensively.
- Methemoglobinemia, in vertebrate erythrocytes, hemoglobin can also be a sensitive target for oxyradical attack.

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**APPENDIX C**  
**BIODEGRADATION PREDICTIONS FOR FUEL OXYGENATES**

Alfredo A. Marchetti and David Layton  
Health and Ecological Assessment Division  
Lawrence Livermore National Laboratory  
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## **Introduction**

Biodegradation is the process by which a chemical is destroyed or transformed by living organisms—primarily bacteria and fungi. It can be the main removal mechanism of a contaminant in the environment, particularly in the subsurface. A chemical that resists biodegradation can accumulate or persist in soils, sediments, as well as surface and ground water. Typical examples of recalcitrant (i.e., resistant to biodegradation) chemicals that seriously affected the environment are DDT and branched alkyl detergents.

The introduction of MTBE as a gasoline additive to reduce air pollution and improve octane number unintentionally resulted in ground water contamination because of its limited biodegradation potential and relatively high water mobility. Concerns over water contamination have prompted the state of California to implement a phase out of MTBE in gasoline, which may extend to the rest of the nation in the future. Given this background, it is clear that the potential for biodegradation should be an integral part of the evaluation of candidate oxygenates for diesel fuel.

Experiments can be used to evaluate the potential of a compound to biodegrade, however, realistic biodegradation tests are too slow and laborious to be applied practically to a large number of candidate compounds. It is more efficient to start with a relatively quick elimination of unlikely candidates. For this purpose, a predictive approach can be used to separate compounds that are most likely to be recalcitrant from those that are most likely to be biodegradable. Predictions can be made based on structural similarities to compounds whose behavior is known. For example, the following structures or groups in a molecule generally increase the resistance to aerobic biodegradation<sup>i</sup>:

- Halogens, especially chlorine and fluorine
- Chain branching, especially quaternary carbon and tertiary nitrogen, or extensive branching
- Nitro, nitroso, azo, arylamino groups
- Polycyclic residues (polycyclic aromatic hydrocarbons or PAHs), especially with more than 3 fused rings
- Heterocyclic residues
- Aliphatic ethers (C-O-C) bonds

On the other hand, the presence of groups in a molecule that are normally found in natural products, such as esters and acids, normally indicate that the compound will be easy to biodegrade. Models can be designed to predict the biodegradability of a compound based on its chemical structure by establishing quantitative structure-activity relations. The premise of this type of model is that the activity in question, in this case biodegradation, is a function of the contribution of selected fragments or chemical substructures that form the molecule.

Here we present the results of prediction models for a group of compounds, including oxygenates being considered as diesel fuel additives. We start with a description of the biodegradability model; then, we present the results of the model calculations for the compounds in question. Finally, we present a more detailed assessment on the biodegradation of two of the top candidates (i.e., tripropylene glycol ether and tributyrin). Biodegradability Probability Program

The Biodegradation Probability Program (BIOWIN v4.0)<sup>ii</sup> estimates the probability of a compound to biodegrade under aerobic conditions. The program generates predictions from six regression models. Two of the models (linear and nonlinear) are based on critically reviewed biodegradation data for a set of 295 chemicals. These data consist of screening tests, biological treatment simulations, grab sample tests with soil or water, and field studies. The compounds were assigned a binary indicator variable of 1 or 0 depending on their capacity to biodegrade rapidly or not, respectively. From the 295

chemicals, 186 were reviewed as readily biodegradable. A total of 36 chemical substructures and the molecular weight were selected as regression variables. A matrix of 295 chemicals by 37 descriptors (36 chemical fragments plus molecular weight) was generated along with a matrix of 295 chemicals by 1 biodegradation variable (1 or 0). Multiple linear and nonlinear regressions were performed with these matrices to determine the coefficient corresponding to each descriptor. The probability of biodegradation in the linear model is given by the following equation:

$$Y_j = Ao + \sum_{i=1}^{36} Ai \cdot Fi + Am \cdot M$$

- $Y_j$  = probability that chemical  $j$  will biodegrade
- $Fi$  = number of times  $i^{\text{th}}$  substructure appears in chemical  $j$
- $Ao$  = intercept
- $Ai$  = regression coefficient for  $i^{\text{th}}$  substructure
- $M$  = molecular weight of chemical  $j$
- $Am$  = regression coefficient for  $M$

The regression coefficients were calculated using the least squares method. For the nonlinear model the probability equation is the following:

$$Y_j = \exp(Ao + \sum Ai \cdot Fi + Am \cdot M) / [1 + \exp(Ao + \sum Ai \cdot Fi + Am \cdot M)]$$

In this case, the coefficients were calculated using the maximum likelihood method, because the model is not a linear function of the unknown coefficients. In either model, if the probability of biodegradation is more than 0.5, the compound in question is considered readily biodegradable.

The Japanese Ministry of International Trade and Industry (MITI) has designed a testing protocol (MITI-1) to screen substances for biodegradation under aerobic conditions in an

aqueous medium. A large number (~900) of discrete substances have been tested using this protocol, which therefore provides a large database that can be used for evaluating relationships between chemical structure and biodegradation potential. A linear and a nonlinear MITI biodegradation model are included in BIOWIN v4.0. The MITI models employ a set of 884 chemicals from the MITI database; 385 of the 884 chemicals were evaluated as readily biodegradable and assigned a binary indicator variable of 1. The 884 compounds were divided into a training dataset (589 compounds) to parameterize the regression, and a validation dataset (295 compounds) to test its effectiveness. The training set was used to derive the coefficients as in the linear and nonlinear models already described. The MITI models use 42 chemical substructures—instead of 36—and the molecular weight as independent variables, but the majority of the fragments are the same as in the previous models.

There are two survey models for primary and ultimate biodegradation included in BIOWIN v4.0 based on the opinions of 17 experts in the field. The experts were asked to survey a number of chemicals in terms of the time required to achieve primary and ultimate biodegradation on a scale of 1 to 5 (1 for persistent, 2 for months, 3 for weeks, 4 for days, and 5 for hours). The ratings were then averaged for each chemical and a matrix was formulated for both primary and ultimate biodegradation using the 36 fragments and molecular weight parameter of the linear and nonlinear models. Using the average ratings from the experts as the solution matrix, linear regressions were performed to evaluate the coefficients for the various substructures and molecular weight.

Regarding the accuracy of the models, calculations for the 295 chemicals that form the database of the linear and nonlinear models show that the nonlinear model predicts correctly 93.2% of the time if the chemical biodegrades fast (probability > 0.5) or not (probability < 0.5). In the case of the MITI nonlinear model, the predictions are correct 82.9% of the time for the training set and 80.7% of the time for the validation set.

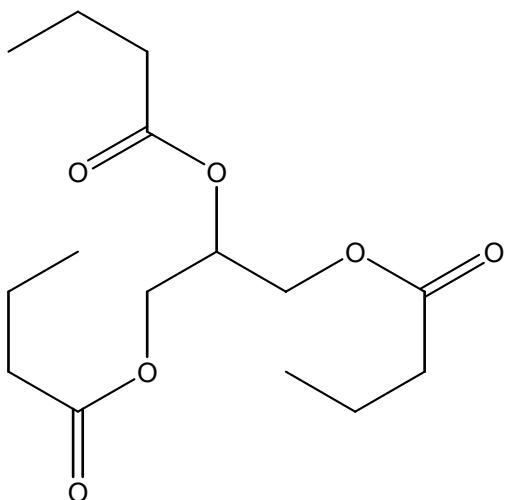
## Results and Discussion

We ran the BIOWIN program for 15 oxygenates and 4 of the typical hydrocarbons found in fuels. Figures 1 and 2 show the biodegradation probability (horizontal bars) calculated using the nonlinear and the MITI nonlinear models, respectively. The vertical line at probability 0.5 represents the limit between readily biodegradable ( $>0.5$ ) or not ( $<0.5$ ). Both models agree in the classification of 13 out of the 19 compounds. The nonlinear model predicts that 11 out of the 19 compounds biodegrade readily, while the MITI nonlinear model predicts that 16 of the compounds biodegrades readily. This is not surprising because the MITI database is indicative of very aggressive biodegradation conditions. In contrast, the database used for the nonlinear model entails more diverse biodegradation conditions.

Overall, the nonlinear model seems to represent better the behavior of a compound in the environment than the MITI nonlinear model. For example, the MITI nonlinear model predicts that most of the ethers including MTBE will biodegrade more or less readily (probability~0.6) in the environment, which is contrary to what would be expected from experience. On the other hand, the nonlinear model calculates a probability of biodegradation of less than 0.1 for all the ethers in the list. Then, ethyl benzene is classified as readily biodegradable by the nonlinear model (probability~1.0) and as not readily biodegradable by the MITI nonlinear model (probability~0.5). In experiments, ethyl benzene has been found to biodegrade fast. It may be possible that the conditions of the MITI test protocol do not represent well the average conditions found in the environment for biodegradation. As a caveat, these models are based on binary regressions and classifications as biodegradable or not become less reliable as values approach 0.5. Both models predict that esters are most likely to be readily biodegradable, which is also in agreement with experimental observations. Therefore, from the list of oxygenates, the ones more likely to biodegrade fast in the environment are: (1) tributyrin, (2) dibutyl maleate, (3) diethyl adipate, and (4) 2-ethoxyethyl acetate. Both the nonlinear and the MITI-nonlinear models classify these oxygenates as readily biodegradable with probabilities close to 1.0.

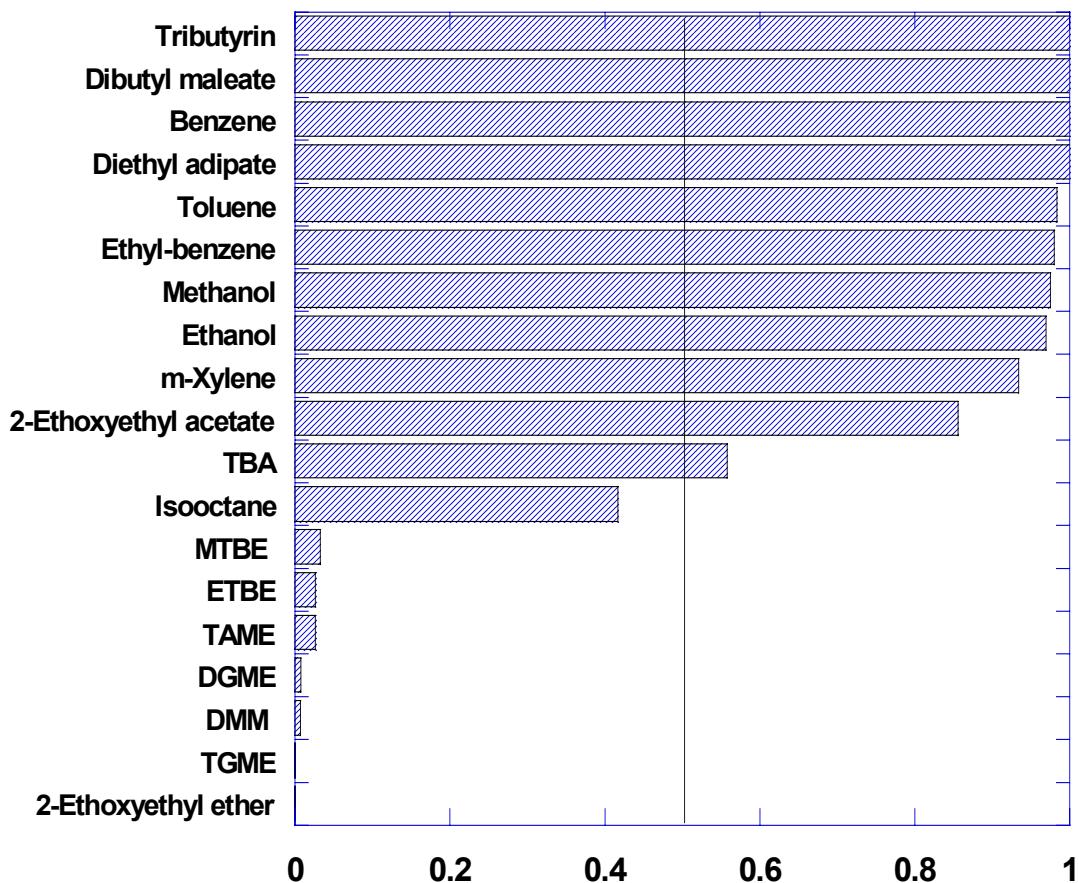
### ***Biodegradation of TGME and Tributyrin***

We could not find any experimental data on the biodegradation of tripropylene glycol monomethyl ether (TGME) or tributyrin; hence, this is only a predictive evaluation. Tributyrin is a molecule with three ester groups. In general, esters biodegrade easily in the environment. In addition, both the non-linear and MITI non-linear models of BIOWIN v4.0 predict a high probability of biodegradation for tributyrin (probability ~1.0). Therefore, it appears that tributyrin would be biodegraded readily in the environment. However, these models are based on molecular fragment addition and may not be sensitive to steric effects, i.e., the arrangement of atoms in space. It is difficult to predict without further investigation whether the tributyrin peculiar arrangement of ester groups (shown below) could significantly affect biodegradability one way or the other.



Tributyrin

## Biodegradation Probability (nonlinear model)



TBA = Tert-butyl alcohol

MTBE = Methyl tert-butyl ether

ETBE = Ethyl tert-butyl ether

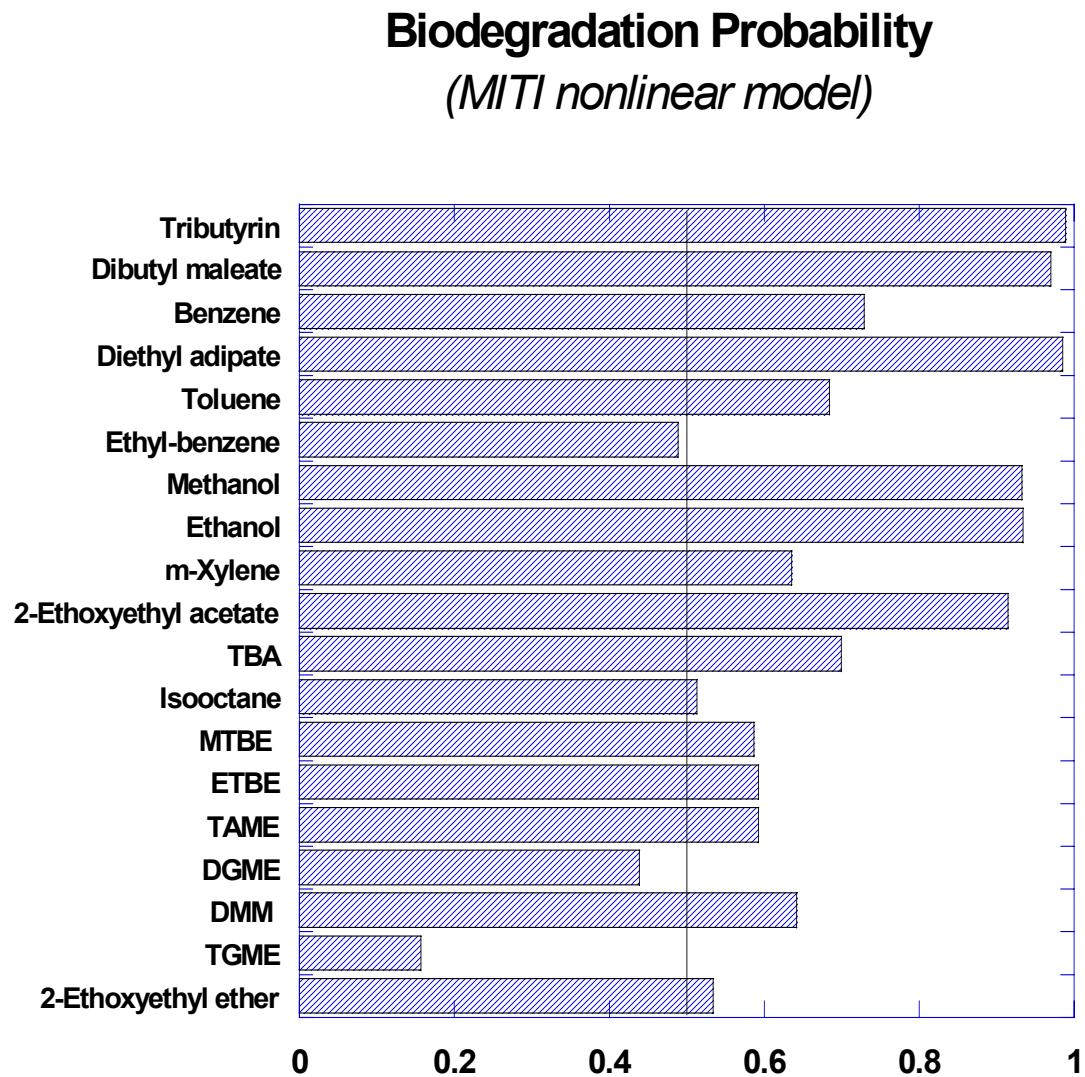
TAME = Methyl tert-amyl ether

DGME = Dipropylene glycol monomethyl ether

DMM = Dimethyl methoxy ether

TGME = Tripropylene glycol momomethyl ether

Figure C-1. Predictions of biodegradation probability using the program BIOWIN v4.0. The results correspond to the nonlinear model. The vertical line at probability 0.5 represents a hard limit for the classification of a compound as readily biodegradable ( $>0.5$ ) or not ( $<0.5$ ).



TBA = Tert-butyl alcohol

MTBE = Methyl tert-butyl ether

ETBE = Ethyl tert-butyl ether

TAME = Methyl tert-amyl ether

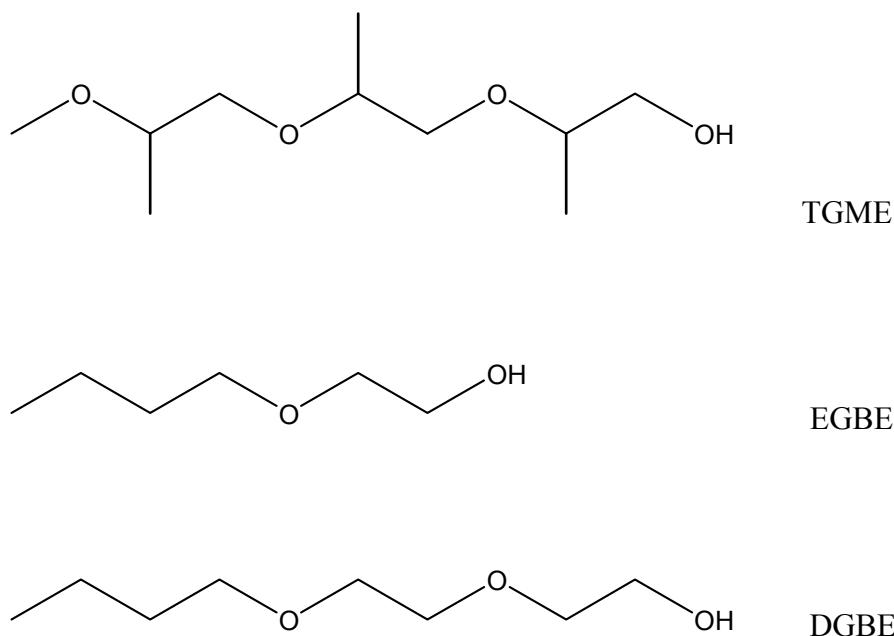
DGME = Dipropylene glycol monomethyl ether

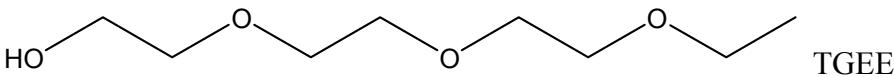
DMM = Dimethyl methoxy ether

TGME= Tripropylene glycol momomethyl ether

Figure 2. Predictions of biodegradation probability using the program BIOWIN v4.0. The results correspond to the nonlinear model for the MITI database. . The vertical line at probability 0.5 represents a hard limit for the classification of a compound as readily biodegradable ( $>0.5$ ) or not ( $<0.5$ ).

TGME (a glycol ether) is a molecule that combines an aliphatic alcohol group ( $-OH$ ) and three aliphatic ether groups ( $C-O-C$ ). That is a combination of one relatively biodegradable and three relatively recalcitrant fragments. Calculations using BIOWIN v4.0 indicate that TGME is not readily biodegradable in both the non-linear and MITI non-linear models (probability  $<0.5$ ). To put this result in context, we ran BIOWIN v4.0 for other glycol ethers for which we found experimental data. They are ethylene glycol monobutyl ether (EGBE), diethylene glycol monobutyl ether (DGBE), and triethylene glycol ethyl ether (TGEE). The chemical structures of TGME, EGGE, DGBE, and TGEE are shown below.





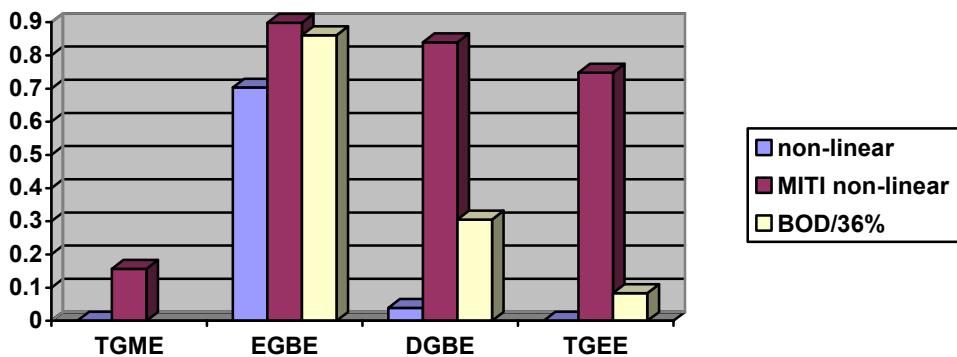
The results are summarized in Table 1. The non-linear model predicts that EGBE is readily biodegradable but DGBE and TGEE are not. On the other hand, the MITI non-linear model predicts that all three are readily biodegradable.

Table 1. Biodegradation predictions

Name	CAS #	Formula	MW	Non-linear model <sup>(*)</sup>	MITI linear <sup>(*)</sup>
Tri-propylene glycol monomethyl	25498-49-1	C <sub>10</sub> H <sub>22</sub> O <sub>4</sub>	206.28	0.0001	0.1571
Ethylene glycol monobutyl ether	111-76-2	C <sub>6</sub> H <sub>14</sub> O <sub>2</sub>	118.18	0.7032	0.8982
Diethylene glycol monobutyl ether	112-34-5	C <sub>8</sub> H <sub>18</sub> O <sub>3</sub>	162.23	0.0395	0.8400
Triethylene glycol ethyl ether	112-50-5	C <sub>8</sub> H <sub>18</sub> O <sub>4</sub>	178.23	0.0002	0.7482

<sup>(\*)</sup>Results obtained using BIOWIN v4.0, a probability < 0.5 indicates in general that the compound does not biodegrade readily.

The experimental data consisted of measurements of biochemical oxygen demand after 5 days of incubation (BOD<sub>5</sub>) published by Bridie et al.<sup>iii</sup> in 1979. The results in percent of the total theoretical oxygen demand (%thOD) are 31% for EGBE, 11% for DGBE, and 3 % for TGEE. To compare to the model predictions, we tried a normalization of the experimental results. By roughly following the guidelines of the Organization for Economic Cooperation and Development, a biodegradation test result of 60% removal of the compound in 10 days would indicate that the compound is readily biodegradable. We assumed a first order biodegradation process and that the %thOD represented the fraction of compound degraded; then, a 36% thOD at 5 days would indicate a readily biodegradable compound equivalent to the 60% degradation at 10 days. Subsequently, we set an arbitrary scale where 0% represents 0 probability of biodegradation and 36% a probability of 1 by dividing the experimental %BOD<sub>5</sub> values by 36%. The results of this normalization are shown in the following plot along with the model predictions.



With this normalization, the experimental results fall between the predictions of the non-linear and MITI models. Using the value 0.5 as the marker to divide readily biodegradable and not categories, the non-linear model predicts correctly the experimental data for all 3 glycol ethers, while the MITI non-linear agrees only with EGBE. Note that the MITI database represents more aggressive biodegradation conditions. Considering the predictions of both models, it would appear that TGME would not be readily biodegraded in the environment. This conclusion would also be supported by the trend of the experimental data, i.e., BOD decreases going from EGBE to TGEE (lighter to heavier molecule, 1 to 3 ether groups). TGME has a higher molecular weight than the other compounds and methyl branching; these factors are known to inhibit biodegradation.

A final assessment of the potential for biodegradation of both tributyrin and TGME will require experimental tests.

## References

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Howard, P.H., et al. 1992. Predictive Model for Aerobic Biodegradability Developed from a File of Evaluated Biodegradation Data. *Environ. Toxicol. Chem.* 11:593-603.

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<sup>iii</sup> Bridie, A.L., et al. 1979. *Water Res.* 13, 627-630.